Energy, Mines and Resources Canada / Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

CANMET ACIDIFICATION/VOLATIZATION/RENEUTRALIZATION PROCESS FOR CYANIDE RECOVERY AND ENVIRONMENTAL POLLUTION CONTROL

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March 1985

Project MRP-3.5.0.2.04
Effluent Treatment

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66 pp

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT MRP/MSL 85-44 (IR)

MICROMEDIA

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CANMET ACIDIFICATION/VOLATIZATION/RENEUTRALIZATION PROCESS FOR CYANIDE RECOVERY AND ENVIRONMENTAL POLLUTION CONTROL

by

V.M. McNamara

EXECUTIVE SUMMARY

An investigation was carried out at CANMET to define the many advantages which can accrue from the application of an unsophisticated acidification/volatilization process to cyanide and metals recovery from a representative gold mill barren bleed. The test solution was obtained from the circuit of a participating mill.

The cyanide concentration in the bleed was 375 mg/L and was 75% complexed by the following metal content: Zn, Ni, Cu and Fe were present at levels of 50, 40, 65 and 18 mg/L respectively. The thiocyanate concentration was 295 mg/L. The quantity of this solution which would require treatment at the mill site is approximately 1000 tonnes per day.

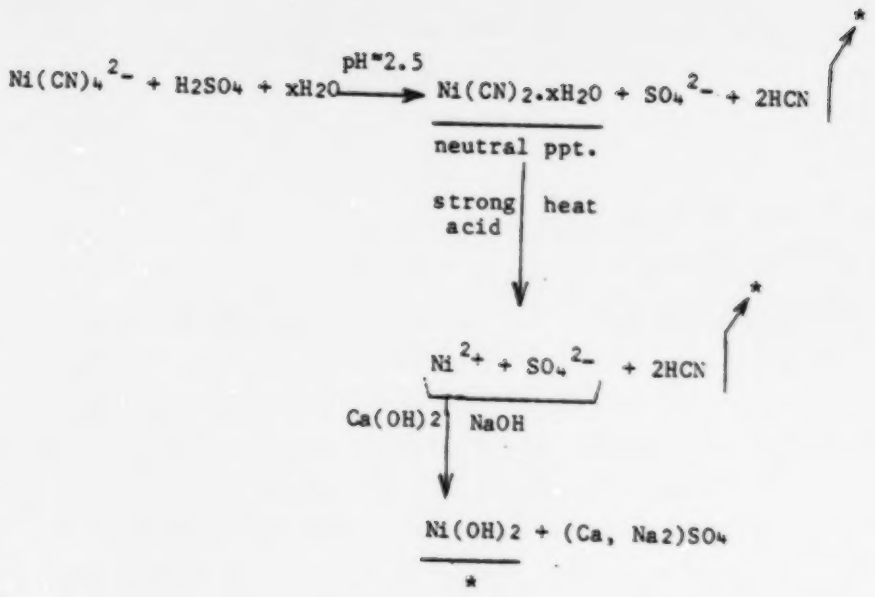
A continuous-flow bench-scale reactor assembly was designed to test various parameters associated with classical acidification methodology. The steps incorporated into the substantially modified version have been designated as the AVR process (Acidification/precipitation; Volatilization and re-absorption of all liberated HCN for reuse; Reneutralization of the waste water and recovery of metals).

The following reactions represent, concisely, the steps in the process. The basis is one metallocyanide complex.

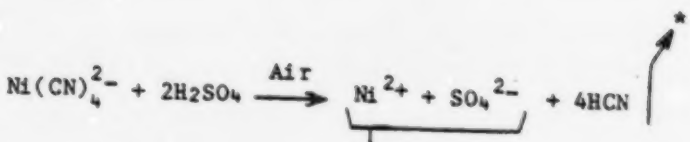
a) Acidification/precipitation

$$Ca(CN)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCN \uparrow^{*}$$

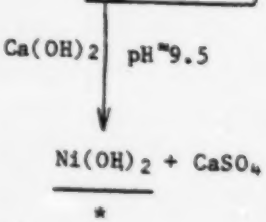
*All cyanide and all non-ferrous metal recovered.



b) Volatilization via intensive aeration.



c) Reneutralization



The H_2SO_4 requirement was ≈0.9 kg/tonne barren bleed. Reneutralization required ≈0.5 kg $Ca(OH)_2$/tonne.

Other acidification reagents tested were H_2SO_3 and SO_2 gas. They were equally effective for the achievement of HCN evolution and neutral-complex precipitation. No cyanate ion was formed.

Process barren effluent, after solid/liquid separation, contained about 1 mg/L metal cyanide. A simple "polishing" technique is suggested. Other "in situ" methods are being evaluated. The process does not result in the addition of a toxic component to the final waste nor does it redirect toxicity from one form to another for discard.

The value of recovered cyanide is substantially greater than process reagent costs. Precipitate treatment ensures that toxic metal cations do not report to the waste, and enables recovery of the metals (as a sulphate solution) for process stoichiometry control if required, or as an iron-free oxide concentrate for periodic shipment to a metal processor.

An empirically derived treatment parameter (AVR.TP) can be used as a guide for the potential applicability of this cyanide recovery process.

TP = tonne waste water to be treated per one kg total cyanide content (CN_T) in the water.

If TP<3 AVR should be very seriously considered for application. Positives are pervasive. Should be pilot tested.

If 3<TP<5 AVR should be considered as a potentially applicable process and be carefully considered.

If TP>5 Destructive oxidation processes, or ion exchange, would appear to be more appropriate.

Finally, reverse osmosis (RO) is an emerging technology for application to hydrometallurgical waste water problems. If RO methodology proves to be technically and economically feasible, then it would have a very positive impact on the treatment parameter. AVR capital costs relate primarily to volume of water to be treated. An optimized RO concentration factor of, say, 5 would greatly decrease plant size requirements.

PROCÉDÉ ACIDIFICATION/VOLATILISATION/RENEUTRALISATION DE CANMET POUR LA RÉCUPÉRATION DU CYANURE ET LE CONTRÔLE DE LA POLLUTION ENVIRONNEMENTALE

par

V.M. McNamara

SOMMAIRE
À L'INTENTION DE LA HAUTE DIRECTION

Une étude a été effectuée à CANMET afin de définir les nombreux advantages pouvant découler de l'application d'un procédé simple d'acidifcation et de volatilisation pour la récupération de cyanure et des métaux à partir d'un effluent stérile représentatif, dans une usine de traitement de l'or. La colution d'essai a été obtenue à partir du circuit d'une usine de traitement participante.

La concentratqion de cyanure dans l'effluent était de 375 mg/L et était composée à 75 % des métaux suivants: Zn, Ni, Cu et Fe avec des teneurs respectives de 50 mg/L, 40 mg/L, 65 mg/L et 18 mg/L. La concentration de thiocyanate était de 295 mg/L. La quantité de cette solution qui devrait être traitée à l'usine est d'environ 1 000 tonnes par jour.

Un montage de réacteur de laboratoire à écoulement continu a été conçu afin de faire l'essai de divers paramètres associés à la méthodologie classique d'acidification. Les étapes incorporées à la version considérablement modifiée ont été désignées sous le nom de procédé AVR (Acidification"précipitation; Volatilisation et réabsorption de tous les HCN libérés afin de les réutiliser; Reneutralisation des eaux usées et récupération des métaux).

Les réactions suivantes représentent, de façon concise, les étapes du procédé. La base est un complexe de métallocyanure.

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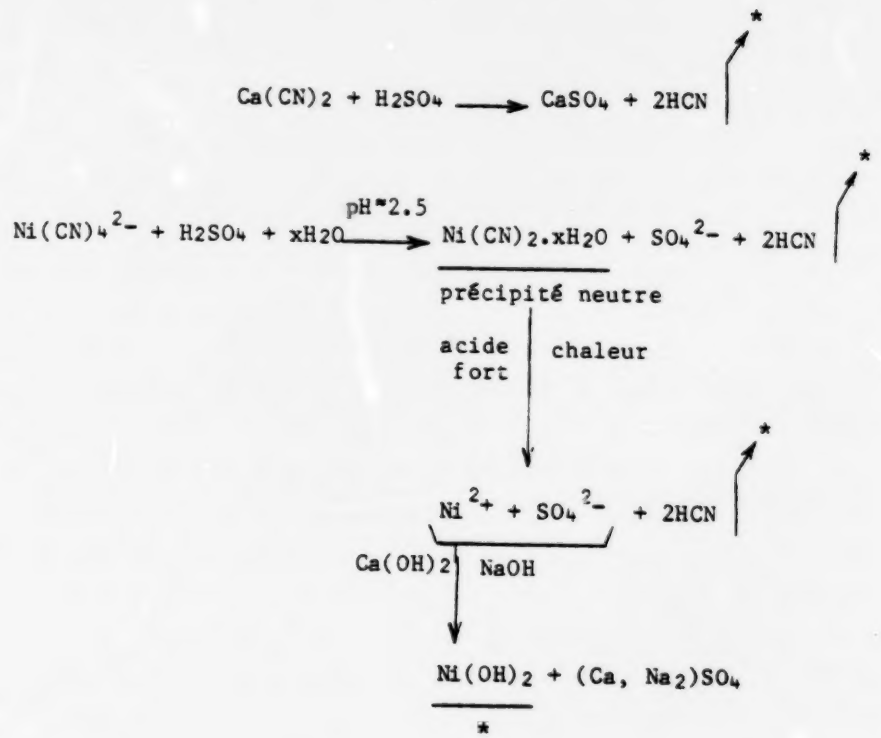
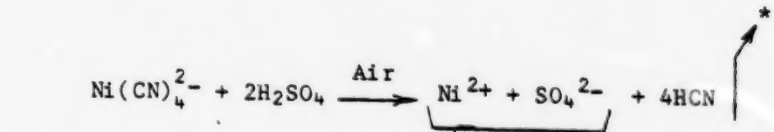
*Tout le cyanure et tous les métaux non ferreux ont été récupérés

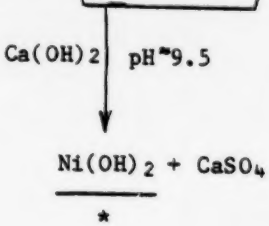
a) Acidification/précipitation


Ca(CN)2 + H2SO4 → CaSO4 + 2HCN ↑*
Ni(CN)4 2- + H2SO4 + xH2O pH≈2.5 → Ni(CN)2.xH2O + SO4 2- + 2HCN ↑*
précipité neutre
acide fort
chaleur
Ni 2+ + SO4 2- + 2HCN ↑*
Ca(OH)2 NaOH
Ni(OH)2 + (Ca, Na2)SO4
*

b) Volatilisation par aération intensive



c) Reneutralisation



Le besoin en H_2SO_4 était d'environ ≃0,9 kg par tonne d'effluent stérile. Pour la reneutralisation, il était d'environ ≃0,5 kg $Ca(OH)_2$/ tonne.

Les autres réactifs d'acidification testés sont les gaz H_2SO_3 et SO_3. Ils étaient tout aussi efficaces pour l'évolution du HCN et la précipitation neutre-complexe. Aucun ion de cyanure ne s'est formé.

L'effluent stérile du procédé, après la séparation des solides et des liquides, contenait environ 1 mg/L de cyanure de métal. On suggère une simple technique de "polissage". D'autres méthodes "in situ" sont actuellement à l'étude. Le procédé n'a pas pour conséquence d'ajouter un élément toxique au résidu final ni de rediriger la toxicité d'une forme à une autre pour fins d'élimination.

La valeur du cyanure récupéré est largement supérieure au coût des réactifs du procédé. Le traitement par précipitation garantit que les cations métalliques toxiques ne sont pas présents dans les résidus et il permet la récupération des métaux (en solution de sulfates) pour le contrôle automatique de la stoechiométrie au besoin, ou en concentré d'oxyde ne contenant pas de fer et envoyé périodiquement à une société qui achète ce concentré en vue de le traiter.

Un paramètre de traitement (AVR.TP) obtenu de façon empirique peut être utilisé comme guide pour l'applicabilité possible de ce procédé de récupération du cyanure.

TP = tonne d'eau usée à traiter pour chaque kilogramme de cyanure au total (CN_T) contenu dans l'eau.

Si TP<3 On devrait considérer sérieusement l'application du procédé AVR.

On devrait en faire l'essai en usine pilote.

Si 3<TP<5 On devrait considérer l'application possible du procédé AVR avec prudence.

Si TP>5 Les procédés d'oxydation destructifs, ou l'échange d'ions sembleraient plus appropriés.

Enfin, l'osmose inverse (RO, Referse Osmosis) est une nouvelle technologie qui s'applique aux problèmes des eaux usées hydrométallurgiques. Si la méthodologie de l'osmose inverse s'avère techniquement et économiquement faisable, elle aurait alors des repercussions très positives sur le paramètre de traitement. Les coûts en capital de l'AVR dépendent surtout du volume d'eau à traiter. Un facteur de concentration optimisé d'osmose inverse de 5, par exemple, réduirait considérablement les exigences quant à la dimension des installations.

INTRODUCTION

Several Canadian gold producers must discard or "bleed", daily, large tonnages of barren solution from the zinc precipitation circuit. This barren filtrate bleed is normally directed to a tailings pond. Due to the relatively high content of both "free" cyanide ion (present as NaCN or $Ca(CN)_2$ reagent) and base metal complexes of cyanide (principally Cu, Ni, Zn and Fe species) in this effluent, it became apparent that the risk to the environment via pond outflow to the watershed was of a magnitude that might not be acceptable. The "free", or available, cyanide content of the filtrate from the filter press encourages recycling to the leach circuit. However, the bleed is necessitated in order to prevent the build-up of unacceptable levels of inhibitors affecting various stages of the gold recovery process.

A decade ago, CANMET and six cooperating gold mills initiated an increased R & D effort directed toward establishment of a best practicable technology for the treatment of barren bleed for cyanide pollution abatement. Concomitantly, Environment Canada was working toward establishment of guidelines pertaining to the cyanide content which could be tolerated in waste water which was discharged beyond the plant gate as tailings pond overflow. Regulations regarding discharge specifications were necessarily dependent upon the development of adequate technology to control the matrix of complex cyanide-containing pollutants. The results of the R & D program are available in reports which emanated from CANMET (1,2,3,4). The investigations included two treatment methodologies involving cyanide recovery for reuse (AVR (1) and ion exchange (2)). AVR designates the operational package which involves acidification of the barren bleed, volatilization of the HCN formed as the various cyanide-containing compounds dissociate, recovery of the cyanide from the vapour phase by absorption into caustic or lime slurry, and reneutralization of the liquid phase with lime slurry to meet disposal requirements. Figure 1 shows, schematically, the steps in the process. Two alternatives for cyanide control involved destruction of cyanide complexes via the oxidation of cyanide ion to cyanate ion (ozonation (3) and alkaline chlorination (4)).

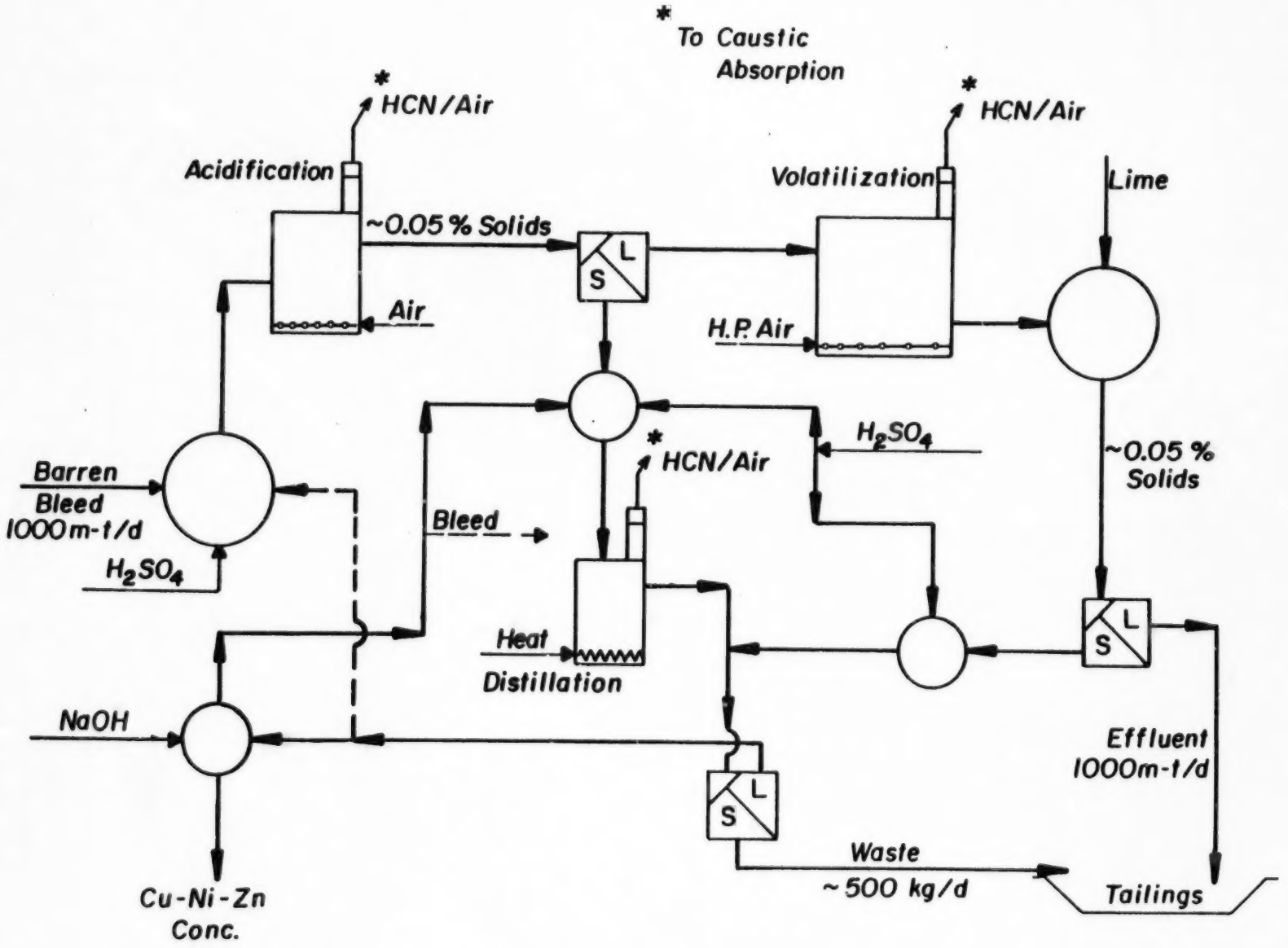


Figure 1 AVR PROCESS SCHEMATIC

In the late 1970's and early 1980's certain gold mills chose to install cyanide destruction processes, particularly alkaline chlorination. In 1982 another oxidative technique was developed (5) which involved the use of SO_2 gas as the oxidizing agent. This method has subsequently been applied at some gold milling operations. Control of pH and oxidation-reduction potential is such that cyanide content is converted to equivalent cyanate ion. The most favourable aspect of these oxidative processes is minimization of capital costs.

It is, however, apparent to an increasing number of gold mill operators that very significant quantities of potentially reusable cyanide can be lost when destructive oxidation processes are applied to the effluent control problem. In some gold mills the recovery of cyanide would quantify as hundreds of thousands of dollars in value per year. Cyanide recovery and reuse can thus repay the additional costs involved in the installation of the AVR cyanide recovery process, which is also capable of delivering a considerably more acceptable net plant discharge. A higher level of pollutant removal from discharged waste is achieved, and no potentially polluting reagent or reaction product is added to the waste.

The application of the CANMET AVR process to the treatment of gold mill barren bleed has been positively presented (1). Several natural bleed solutions were studied, representing a wide range of contaminating metallocyanide species. A significant advantage of the process is that it enables recovery of all of the cyanide content (reported as CN_T) of the barren bleed. Further, with installation of small-scale auxiliary equipment, the non-ferrous base metal content can be readily concentrated for recovery, and the iron disposed of to the tailings pond as innocuous precipitate.

The present investigation involved the application of AVR to one particular gold mill barren bleed. Campbell Red Lake Gold Mines Ltd., of Balmerton, Ontario, supplied the required barren bleed solution. The bench-scale pilot assembly was located at CANMET. The company covered the costs of the required control analysis program, which was carried out under contract by Bondar-Clegg and Company Ltd. of Ottawa, Ontario.

The standard features of the AVR process involve acidification with H_2SO_4 to an optimum pH level (usually 2.4 to 2.5); separation of acid-induced precipitation solids which are primarily metallocyanide neutral

complexes, and from which both the cyanide and metal contents are recovered; intensive aeration of the filtrate in order to efficiently volatilize hydrocyanic acid, thus forcing the dissociation of the soluble but highly stable metallocyanide complexes; recovery of HCN in caustic or lime slurry by passing all reactor off-gases through absorber towers; reneutralization of the fully-aerated effluent with lime prior to discharge to the ponding area. Metal content can also be readily recovered from the "neutral" precipitate formed during the final step of the process.

The current work involved some experiments aimed at establishing the feasibility of using SO_2 gas as an acidification agent, particularly in regard to utilization of off-gases from a gold recovery roasting step. The main basis, however, for the bench-scale continuous-flow feasibility study was the use of sulfuric acid. Reaction times are considerably extended for acidification by diluted SO_2 gas due to the physical limitations imposed by gas to liquid mass transfer rates, particularly under the acidic conditions which normally exist in AVR acidifiers.

Acidification, with concurrent air stripping, of a gold cyanidation process barren bleed, with the objective of economical recovery of cyanide content as absorbable HCN, was a technique employed at Hudson Bay Mining and Smelting Co., Flin Flon, Manitoba for many years (6,7). Perforated plate stripping towers were used. Scale build-up on tower internals by adhering, acid-induced precipitates was a major problem. Precipitates formed during acidification normally have a considerable cyanide content. The recovery of cyanide at this operation was based upon "regenerable cyanide" which was perceived as the quantity evolved during acidification of gold process barren bleed under moderate conditions (i.e., pH 2.5). The objective of the barren bleed treatment did not include the achievement of effluent control at that point in time. Efforts were made in the mid-1970's to modify the system toward environmental control, apparently without success.

The cyanide regeneration method was studied further, in considerable detail, by Avedesian et al at the Noranda Research Centre (8). The specific application was the recovery of cyanide from waste bleed solution from a proposed silver cyanidation circuit. In the development of data for process design, these researchers studied counter-current flow in towers packed with Pall rings. The acidified solution was fed to the towers

without prior solid-liquid separation. The effects of precipitate build-up within the bed were noted, but were not studied in detail. It would appear that, in this application, the precipitate constituents were primarily gypsum and CuCNS. Seventy-eight per cent passed through the tower packing. The input solution contained a very high level of cyanide component (~4 g/L as HCN). Economic considerations lead to a design parameter for the final effluent of 120 mg/L HCN equivalent.

Work carried on at CANMET has enabled a number of modifications to be made to the classical "acidification" method. Fine-tuning of several important steps which are involved in successful utilization of this technology in the 1980's and beyond has lead to the more appropriate process designation, AVR process.

A significant proportion of the cyanide content of the barren bleed is very strongly complexed by base metal components. The three major functions of the AVR methodology are:

i) acidification to dissociate anionic metallocyanide complexes, resulting in the precipitation of neutral cyanide compounds which require stronger acidification at elevated temperatures for further destabilization. The extent of dissociation and precipitation depends mainly on the extent of HCN removal from solution, the amount of acid added, and the parameters selected for controlled acid addition.

ii) volatilization to recover HCN produced by:
   a) aeration of the acidified solution
   b) treatment of the precipitates with strong acid.

iii) reneutralization of the aerated solution to precipitate remaining heavy metal cations prior to discharge of the effluent. The precipitates should be treated further for recovery of nickel and zinc.

PROCESS DISCUSSION

Figure 1 shows the schematic diagram of the process. The precipitation and the aeration aspects of the treatment method require special discussion.

In the gold milling industry the quantities of waste water to be treated can be of the order of hundreds of tonnes per day. It is apparent that the safest, most environmentally acceptable and economical mineral acid available for acidification is sulphuric. This acid has been successfully utilized on a large scale for the express purpose of cyanide recovery from a gold mill barren bleed (6,7). The Mills-Crowe operation at Hudson Bay Mining and Smelting Company predated the advent of tough environmental restrictions applicable to waste water quality. The CANMET AVR process involves a considerably modified application of the Mills-Crowe technology. The objectives of the AVR process development were:

i) to recover for reuse all of the cyanide content of a barren bleed. This involves the cyanide which is characterized as CN_T.

ii) to remove from the barren bleed virtually all of the major metal content (Cu, Ni, Zn, Fe), recover the Cu, Ni and Zn as a concentrate, and dispose of the iron as an innocuous waste.

iii) to encourage the application of recovery and reuse technology to gold milling situations where destructive oxidation techniques for cyanide control result in a lost opportunity to recover cyanide reagent. Quantities can be substantial enough to offset the higher capital costs involved in cyanide recovery, and/or defray operating costs.

iv) to provide a process which does not result in a re-routing of the pollutant load to the environment. No potentially unacceptable solid material is discharged and no problem is posed in regard to potentially toxic anionic or cationic species added to the waste water. The technology can be particularly rewarding for a major milling operation located in an environmentally sensitive area.

v) to provide a technology which presents "windows" for the development and inclusion of auxiliary unit operations which could provide water conservation and control of thiocyanate.

I. ACIDIFICATION AND PRECIPITATION

Acidification of the alkaline barren bleed is controlled to an optimized pH level. This acidity level is determined by experimentation. The three key factors involved are:

i) the barren bleed must be optimized in regard to formation of precipitates. This parameter is solution-specific but is normally achieved within the pH range 2.75 to 3.4 (1).

ii) the final level of acidity must result in the most efficient destabilization of the soluble metallocyanide complexes, at normal temperature and pressure. Experimental work (1) has shown that there is no tangible gain in rates of dissociation of the complex ions, by subsequent aeration, at pH levels below pH ≈ 2.4. The efficiency of HCN-product removal from solution is predicated upon optimization of aeration parameters. Aeration is controlling.

iii) the economics of the process do not favor the use of strong acid conditions (i.e., pH << 2.4), or of heat input, due to the large solution volumes to be treated.

The precipitates are processed for both cyanide and metals recovery.

In an acidic milieu, several of the metallocyanide complexes either partially precipitate individually, or inter-react further, to form stable solids which are hydrated and gelatinous. The composition of the whole precipitate is variable in regard to both species represented and to relative quantities. The components exhibit widely differing stabilities. The composition is dependent primarily upon barren bleed complexity, acidification reagent (eg. H_2SO_4 vs H_2SO_3) and, to a lesser extent, rate of acidification. The single species precipitates, which contain zinc or nickel, could be largely dissociated to yield metal ions and molecular HCN by greatly extended aeration. This is, however, totally impractical. Copper cyanide and iron cyanide(s) interact to form "double" complexes, a solid compound which is extremely stable in weak acid (1), irrespective of aeration intensity. In certain circumstances zinc and iron cyanides may behave similarly.

The iron content of gold mill barren bleed represented one of the major problems in achieving truly satisfactory CN_T levels in total waste discharge via oxidation methodology. It also represents a distinct factor

in the evolution of a cyanide recovery process due to the fact that one gram of iron content immobilizes 2.8 grams of potentially reusable cyanide. In the AVR process a precipitate treatment step enables recovery of all the cyanide content of the precipitate, including that portion complexed as copper, or zinc, ferrocyanide (and/or ferricyanide).

The precipitation phenomena have usually been accorded only speculative interest in the literature, a concern primarily regarding equipment fouling. In the AVR process the precipitation aspect has been directly dealt with for the following reasons:

i) the hydrated precipitate contains a considerable portion of the total cyanide available for recovery. This can amount to 10-15%, dependent upon the CN_T and Me_T (total metal) concentrations in the barren bleed. A strong acid precipitate digestion step (at ~100°C) will allow recovery of the total cyanide content of the precipitate by enabling the complete dissociation of the solid complexes to occur, concomitant with distillation of the HCN. This process step is small scale due to the limited amount of precipitate formed per tonne of barren bleed treated. The precipitate mixture is removed from the acidified barren bleed by standard solid/liquid separation methods.

ii) the precipitate would tend to adhere to aeration reactor internals, gradually forming a scale which can be costly to remove. Some gold mill barren bleeds contain a level of calcium which can result in significant gypsum formation upon acidification. Since this component precipitates along with the hydrated metallocyanide flocs, the scaling problem could become very severe.

iii) the cyanide-containing solid complexes will not dissociate appreciably within the aeration stage. If present they would report to the vapaerator effluent, which proceeds directly to the reneutralization step. Here they would redissolve and thus circumvent the required environmental aspects of the technology as well as limiting the economic viability. The vapaerator is the specialized unit of equipment which is designed to achieve efficient volatilization of the HCN component of the acidified barren bleed, at ambient temperature.

iv) the precipitate will contain a significant portion of the original metal content (Me_T) of the barren bleed. Copper and/or zinc content is a requirement for efficient rejection of the ferrocyanide from solution at the acidification stage, via the formation of insoluble ferro (or ferri) cyanide salts. Anionic ferro/ferricyanides are very stable ($\beta \approx 10^{50}$) and will not dissociate at normal temperature and pressure. There may be occasions where the soluble ferrocyanide content of the bleed is at a level such that the complexing agent(s) (Cu/Zn) are present in insufficient quantity to enable precipitation all of the iron complex to occur. At this time, and controlled empirically by analysis feedback, a copper/zinc dosing reagent may be supplied to the barren bleed prior to, or upon, acidification. This metal requirement would be recyclable, as the metal sulfates, from the precipitate digestion step. Recovered metal not required for recycle is convertible to a high-grade concentrate (iron-free) which can be shipped periodically to a metal processor. This solid concentrate contains Cu, Zn and Ni as the oxides.

v) as will be discussed later, it may be possible to utilize ferrous or ferric iron recycle in order to achieve improved precipitation yield of the Cu/Fe cyanide double complex. Tricyanocuprate (I) appears to be the most stable of the weak acid dissociable metallocyanide anionic complexes.

It is noted specifically that, throughout all investigations carried out thus far, no problem has been encountered in respect to iron cyanide rejection from solution (i.e., solution deferrination). If copper dosing of the barren bleed was required it would be for the purpose of deferrination by enhancement of the precipitation phenomena. No catalytic effect upon the dissociation of metallocyanides to metal cations and cyanide ion would be involved.

Sulphurous acid, or SO_2 gas, should be equally as effective as H_2SO_4 for acidification. This reagent could prove to be economical where either an on-site roasting operation was present or where a crude-sulphur burner was installed. However, it would have to be demonstrated that the reagent savings were not off-set by the requirement for more complex gas-scrubbing reactors to ensure full utilization of the SO_2.

A thorough assessment of a cyanide recovery operation which involved SO_2 gas utilization was presented by Burk and Pettis (9). Although their application related to the treatment of barren bleed resulting from a hot cyanidation leach of a silver-copper ore, the use of SO_2 as an acidification agent was proven technically and economically sound. The following chemical reactions were presented.

$$2NaCN + SO_2 + H_2O \longrightarrow Na_2SO_3 + 2HCN \quad (1)$$

$$Na_2Zn(CN)_4 + 2SO_2 + 2H_2O \longrightarrow ZnSO_3 + Na_2SO_3 + 4HCN \quad (2)$$

$$Na_2Cu_2(CN)_4 + 2NaCNS + 2SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2 + Na_2SO_3 + 4HCN \quad (3)$$

Apparently there was no iron content in the solution from which the cyanide recovery was effected. Noteworthy is the fact that the use of SO_2 involved no reaction in which cyanide oxidized to cyanate.

II. VOLATILIZATION

This stage of the process is achieved by intensive air injection into the acidified barren bleed <u>after</u> precipitate removal. In typical gold mill plant practice the solution volumes are so large that heat input is impractical. Therefore HCN volatilization must be accomplished by the most efficient method of air stripping of the ideally water-soluble molecular HCN, at ambient temperature.

A review of physico-chemical data (10,11) suggested that acidification can destabilize soluble anionic metallo-cyanide complexes only to a limited extent, even though HCN is a very weak acid; for example, at 25°C:

$$Ni^{2+} + 4CN^- \longleftrightarrow Ni(CN)_4^{2-} \; ; \; \beta = 10^{22} \quad (4)$$

$$HCN \longleftrightarrow H^+ + CN^- ; \; K = 10^{-9.3} \quad (5)$$

Despite its volatility (b.p. = 26°C), the desorption of HCN from dilute aqueous solutions must overcome substantial mass transfer resistances at the liquid interface that are caused by the high degree of hydrogen bonding and the ideal solubility of HCN in water. <u>Vigorous aeration</u> in a

bubble reactor was recommended (12), preferrably with microbubble dispersion at elevated temperatures or reduced pressures. The addition of stronger complexing ligands or oxidants to this stage could also assist in destabilizing the metallo-cyanide complexes, but overall process criteria (recoveries, reagent costs, effluent quality) may be adversely affected.

U.V. irradiation has been investigated (1). The controlling effect was discovered to be the dissociation of SCN^- to cyanide ion and sulphur.

CHEMISTRY OF THE AVR PROCESS

The reactions which occur during acidification and subsequent aeration of gold mill barren bleed are, in total, very complex. Air input has only one key function. It acts as an inert gas and ensures the stripping of the HCN from the liquid and the transport of the HCN to the absorbers. Oxidation reactions, if any do occur, are minor and would involve only $Cu^+ \rightarrow Cu^{++}$.

The reactions which result in precipitate formation occur at various pH levels (normally within the pH range 9 → 2.75) when acidification progresses slowly, by design (1). In a process, when H_2SO_4 is the acidification reagent, pH control in the acidifier at 2.4 to 2.5 results in all reactions occurring simultaneously and virtually instantly. Hydraulic residence time in the acidifier can be relatively limited. If greatly extended aeration were carried out at this step, the less stable precipitates would slowly redissolve and dissociate.

The key factors which affect the changes in solution content due to precipitation reactions, beyond the unique quality of each particular mill barren bleed, are:

i) the variety of metal-containing components and their concentrations, both absolute and relative.
ii) the type of acidification reagent (H_2SO_4, H_2SO_3, SO_2 gas, HNO_3 etc.).
iii) the concentrations, both absolute and relative, of the cyanide and the thiocyanate components.
iv) the "background" matrix of the solution, particularly in regard to whether the gold leaching reagent is $Ca(CN)_2$ or NaCN. High calcium levels can result in considerable gypsum content in the precipitate and in a near-saturation level of calcium sulphate in the filtrate.

v) the intensity of aeration (for thorough slurry mixing and purging of HCN) employed during acidification).

vi) the hydraulic residence time in the acidifier(s).

vii) the rapidity of the attainment of control pH within the acidifier(s), particularly when staging of incremental pH adjustments are necessitated, as in the use of SO_2 reagent.

The aeration-volatilization step, accomplished with multiple stage of intensive aeration, should only be done on the clear filtrate after the removal of the precipitate mixture. The latter is most economically and efficiently processed in a separate step.

As will be indicated later, an extremely minute degree of precipitation <u>may</u> occur during the aeration step. It is not a desirable feature because a precipitate which developed in the vapaerator could report, in part, to the final effluent or form a film on equipment internals.

The following reactions show what does occur, and under certain conditions may occur, when gold mill barren bleed is acidified with H_2SO_4 and the released HCN is purged from solution with air. Those reactions indicating precipitate formation occur, almost exclusively, during the acidification step. The purely dissociation reactions, which yield metal ions and molecular HCN, are those which are achieved in the intensive aeration-vaporization step.

$$2NaCN + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCN \qquad (6)$$

$$Na_2Zn(CN)_4 + H_2SO_4 + xH_2O \longrightarrow \underline{Zn(CN)_2.xH_2O}_{\text{white}} + 2HCN + Na_2SO_4 \qquad (7)$$

$$Na_2Zn(CN)_4 + 2H_2SO_4 \longrightarrow ZnSO_4 + 4HCN + Na_2SO_4 \qquad (8)$$

$$Na_2Ni(CN)_4 + H_2SO_4 + xH_2O \longrightarrow \underline{Ni(CN)_2.xH_2O}_{\text{green}} + 2HCN + Na_2SO_4 \qquad (9)$$

$$Na_2Ni(CN)_4 + 2H_2SO_4 \longrightarrow NiSO_4 + 4HCN + Na_2SO_4 \qquad (10)$$

The nickel and zinc cyanide precipitates are moderately stable. They will dissociate extensively under greatly extended agitation by air to yield metal sulphate and HCN.

$$2Na_2Cu(CN)_3 + 2H_2SO_4 \longrightarrow \underline{Cu_2(CN)_2} + 4HCN + 2Na_2SO_4 \qquad (11)$$

cuprous cyanide
white

Gold mill barren bleed normally contains relatively substantial quantities of thiocyanate. It appears to take part in the precipitation of copper to some extent, but in secondary relationship to reaction 13.

$$2Na_2Cu(CN)_3 + 2NaCNS + 3H_2SO_4 \longrightarrow \underline{2CuCNS} + 6HCN + 3Na_2SO_4 \qquad (12)$$

white

Ferrocyanide ion, when present, is the primary precipitant for copper. The reverse is, of course, also true.

$$Na_4Fe(CN)_6 + 4Na_2Cu(CN)_3 + 6H_2SO_4 + xH_2O \longrightarrow \underline{Cu_4[Fe(CN)_6].xH_2O} + 12HCN + 6Na_2SO_4 \qquad (13)$$

cuprous ferrocyanide
brownish red

Ferricyanide precipitation reactions would be similar to those which apply to the ferrous complex, if the former exists at all.

If a source of Cu^{++} ion becomes available in the acidifier, either from partial dissociation of a double complex of copper cyanide (reaction 14) or from oxidation of Cu^{+} to Cu^{++} (reaction 17) or, alternatively, because copper sulfate is recycled by design from the proposed precipitate digestion step, then precipitates of the complexed cupric species could form (Eq. 15, 16).

$$Na2\,[Cu^{++}(Cu^{+}(CN)3)2]^{2-} + 2H2SO4 \longrightarrow \underline{Cu_2(CN)_2} + CuSO_4 + 4HCN + Na_2SO_4 \qquad (14)$$

cuprous cyanide
white

$$Na_4Fe(CN)_6 + 2CuSO_4 + 7H_2O \longrightarrow \underline{Cu_2Fe(CN)_6 \cdot 7H_2O} + 2Na_2SO_4 \qquad (15)$$

cupric ferrocyanide
red-brown

$$2Na_2Cu(CN)_3 + CuSO_4 + H_2SO_4 \longrightarrow \underline{Cu_2(CN)_2} + \underline{Cu(CN)_2} + 2HCN + 2Na_2SO_4 \qquad (16)$$

white — cupric cyanide, yellow-green

Further, reaction 16 could conceivably influence, negatively, the dissociation rates for copper complexes in the vapaerator where a dispersed solid cuprous cyanide would be expected to be relatively stable at normal temperatures.

The intensive aeration in the vapaerator operation may also have an indirect effect on the desired rate of conversion of the very stable soluble metallocyanide component, tricyano cuprate (I) ($B_3 = 10^{27.5}$).

$$2Na_2Cu(CN)_3 + 3H_2SO_4 + 0.5O_2 \longrightarrow \underline{Cu(CN)_2} + CuSO_4 + 4HCN + 2Na_2SO_4 + H_2O \qquad (17)$$

cupric cyanide

Cupric cyanide is not expected to be a stable compound in acidic solution.

$$\underline{Cu(CN)_2} + H_2SO_4 \longrightarrow CuSO_4 + 2HCN \qquad (18)$$

If tricyano cuprate (I) could be efficiently precipitated from solution by complexation with Fe^{2+} or Fe^{3+}, then the requirement for vapaerator hydraulic residence time might be lowered appreciably.

$$4Cu(CN)_3^{2-} + Fe^{2+} \longrightarrow \underline{Cu_4[Fe(CN)_6]} + 6CN^- \qquad (19)$$

cuprous ferrocyanide

An additional chemical consideration is relevant to acidification-induced precipitation as it occurs in the acidifier. In some applications the ferrocyanide was rejected from solution without an equivalent decrease in soluble copper cyanide as would be predicted by reaction 13. Although not established, it is probable that the zinc cyanide complex may

precipitate the iron cyanide under certain conditions. The following solid complexation products are known to exist and the stoichiometry of formation can be assumed. For ferrocyanide precipitation,

$$3Na_2Zn(CN)_4 + 2Na_4Fe(CN)_6 + 6H_2SO_4 \longrightarrow \underline{Zn_3Na_2[Fe(CN)_6]_2} + 12HCN + 6Na_2SO_4 \quad (20)$$

For ferricyanide precipitation, if it is present in the barren bleed,

$$3Na_2Zn(CN)_4 + 2Na_3Fe(CN)_6 + 6H_2SO_4 \longrightarrow \underline{Zn_3[Fe(CN)_6]_2} + 12HCN + 6Na_2SO_4 \quad (21)$$

If the cyanidation reagent is $Ca(CN)_2$ then the complexes will be in the calcium form and acidification may yield a substantial amount of gypsum concurrently with the complexes.

Although the chemistry involved in AVR barren bleed treatment is complex, the precise direction of complexation as regards the precipitation of stabilized compounds does not normally affect process control. However, it can be appreciated that a solid-liquid separation step must be included in the process after the acidification stage. Furthermore, the two most stable, soluble complex components of the barren bleed, iron cyanide and copper cyanide, should be rejected from solution and into the precipitate to the maximum extent possible in order that they can be effectively dissociated, in a concentrated form, under strong acid conditions and at elevated temperature. To effectively achieve this objective it may be necessary, in some cases, to recycle in controlled amount, a portion of the metal cations (principally copper) which have been obtained from the precipitate dissociation procedure.

The chemistry of the barren bleed has been discussed at some length. It is important that the decision-makers in the gold processing industry are aware of the chemical complexity which is unique to the cyanide ligand when it is in association with common base metals (13). A significant portion of the cyanide content of the filter press barren will "release" to the gas phase most reluctantly. Efficient cyanide recovery is not predicated solely upon simplified acidification coupled with air purging.

The barren bleed, as shipped from the mill site to CANMET, was analyzed for components of interest to the project. Table 1 shows the results.

Table 1. Analysis of Gold Mill Barren Bleed (mg/L)

CN_T = 375	Zn = 50	Co = 0.56
CNS = 295	Cu = 65	Au = 0.09
CNO = 4	Ni = 40	As = 0.70
SO_4 = 437	Fe = 18	S_T = 188
	Ca = 96	

On the basis of calculated stoichiometry the cyanide complexed by the major metal components would be 280 mg/L, or 75% of the recoverable cyanide from full AVR treatment.

If this solution was "filter fresh" it may have reported a CN_T content of, say, 500 mg/L. That is, the free or uncomplexed cyanide could be much higher than the 95 mg/L estimated herein. This means that it is very advantageous to run a pilot-plant campaign utilizing barren bleed that has not undergone ageing.

Figure 2 shows a flow diagram of the AVR process. It indicates an approximate input-output material balance for the key chemical compounds involved in the system. An assumption, which is realistic, is that the barren bleed is fresh from the mill filter press and contains a significant quantity of "free" cyanide (uncomplexed by metals). Also assumed is an overall cyanide loss of 10%, distributed across the processing scheme.

The selection of two operating shifts per day is quite arbitrary and is based upon a process feed rate of 250 IGpm. The third shift could be keyed to precipitate treatment for metals recovery. Precipitate treatment consists of a combination of leaching (for metal recovery) and distillation (for cyanide recovery) and will be expanded in detail in a subsequent report.

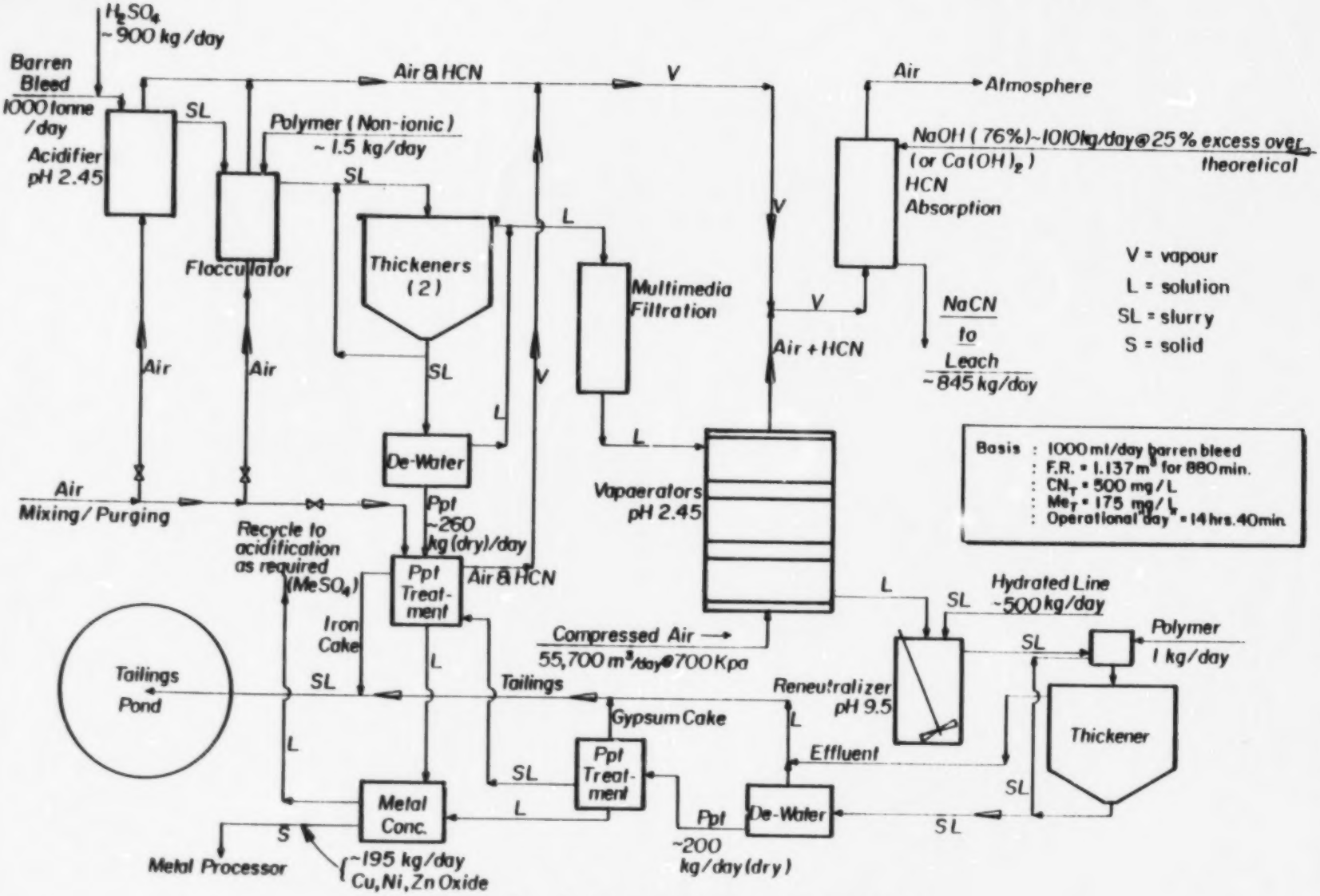


Figure 2 FLOW DIAGRAM - AVR PROCESS

Air for mixing/purging at the acidification stage is obtainable from the standard mill compressor system, already in place. High volume compressed air for dissociation of anionic metallocyanide species in the vapaerators will require a special compressor (discussion and data later). The process overall will be described in considerable detail under subsequent sub-titles for Economic Considerations.

LABORATORY EXPERIMENTATION

Two reagents were chosen for acidification of the barren bleed in the operation of the semicontinuous flow AVR assembly, at steady state conditions. They were:

1. H_2SO_4 - diluted to a concentration of 100 g/L to enable adequate metering rates.
2. SO_2 - water containing 82 g SO_2 equivalent per litre (saturated solution).

Preliminary experimental work clearly indicated that, if SO_2 were to be employed as either a dilute gas (3% by volume in air) or as a concentrated solution in water, the acidification reactor design would require provision for very efficient contacting of SO_2-laden off-gases with the barren bleed. It is necessary to utilize the SO_2 completely so that it will not report to the HCN absorbers. The latter result would decrease process efficiency and increase reagent costs.

The aeration-volatilization reactor (vapaerator) and the reneutralizer unit operations are basically unaffected by the choice of reagent.

I. ACIDIFICATION

1. Sulphuric Acid Mode

Figure 3 shows the reactor assembly used for this experiment. Two vapour-sealed acidifiers (A1 and A2) in series were used to ensure that short-circuiting of the input barren bleed did not occur. Air, entering via dispersers located just above magnetic stirrers, had a dual purpose; thorough mixing of the precipitate slurry and purging of the released HCN

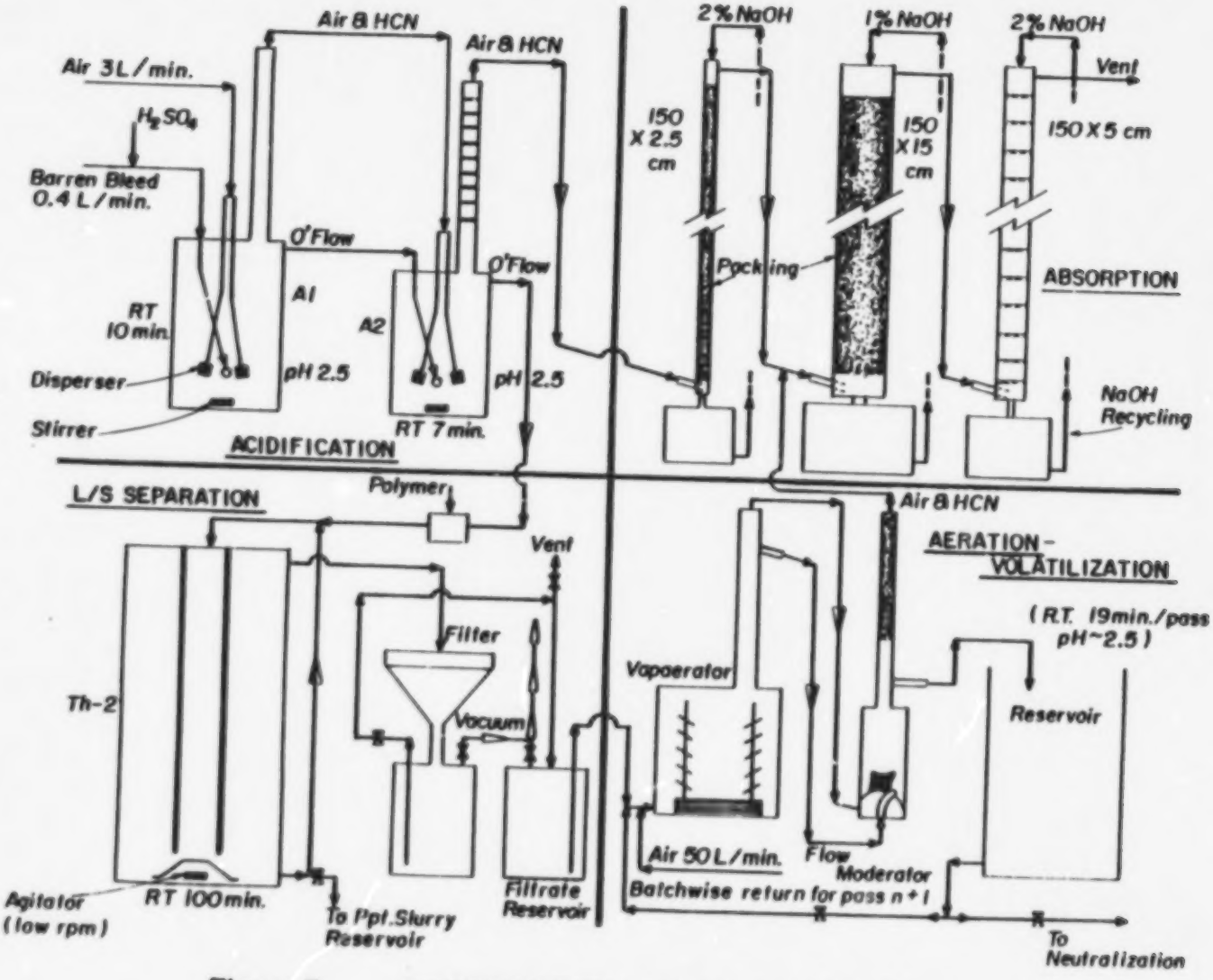


Figure 3 EXPERIMENTAL REACTOR ASSEMBLY

vapour. Barren bleed flow rate was 0.4 L/min to reactor A1. Total nominal hydraulic retention time was 17 minutes. The diluted acid was pumped into the feed inlet line at a rate that averaged 3.64 mL/min. The air agitation/purge rate was 3 L/min (0.25 $m^3/m^2/min$). The pH was monitored at acidifier A1 by rapid recirculation of the slurry through an auxiliary electrode-containing jar. The acidity control in the acidifiers was maintained at pH 2.5 by manual adjustments to an acid metering pump.

The off-gas was directed to a 2.5 cm dia. packed column with recirculating caustic solution as the absorbant. The acidifier outflow slurry was directed to a sealed centre-well thickener (Th-1; not shown); polyelectrolyte was added, as required, to a small in-line mixer through which the slurry passed just prior to entering the thickener. Densified thickener underflow was, in part, continuously recycled to the mixer outflow line. Underflow sludge was also pumped to storage. The #1 thickener off-vapours were vented to the HCN absorber via the acidifier off-gas header.

The #1 thickener overflow went to a larger centre-well backup thickener (Th-2) which was open to the atmosphere. The overflow from this vessel was filtered on an open Buchner for the purpose of yielding a clarified filtrate for vapaerator feed.

The total residence time in the thickener was about 100 minutes. The clarifying "filter-aid" collected a very small proportion of the total precipitate.

2. Sulphurous Acid Mode

Figure 4 shows the extent of advanced modifications which were developed in order to efficiently utilize the available SO_2 content of the prepared sulphurous acid. The reagent was obtained by bubbling SO_2 gas through water in a packed column operating on recycle until the water was saturated by the gas.

Preliminary experiments had indicated that the direct use of diluted SO_2 gas, simulating a roaster off-gas (3% v/v), would require an extensive scrubbing-column system which would involve counter-current flow of barren bleed and SO_2/HCN-laden off-gases. It represents an intriguing prospect for a future development campaign. However, it would appear that the excessive volume of diluent gases, comprising greater than 97% of roaster

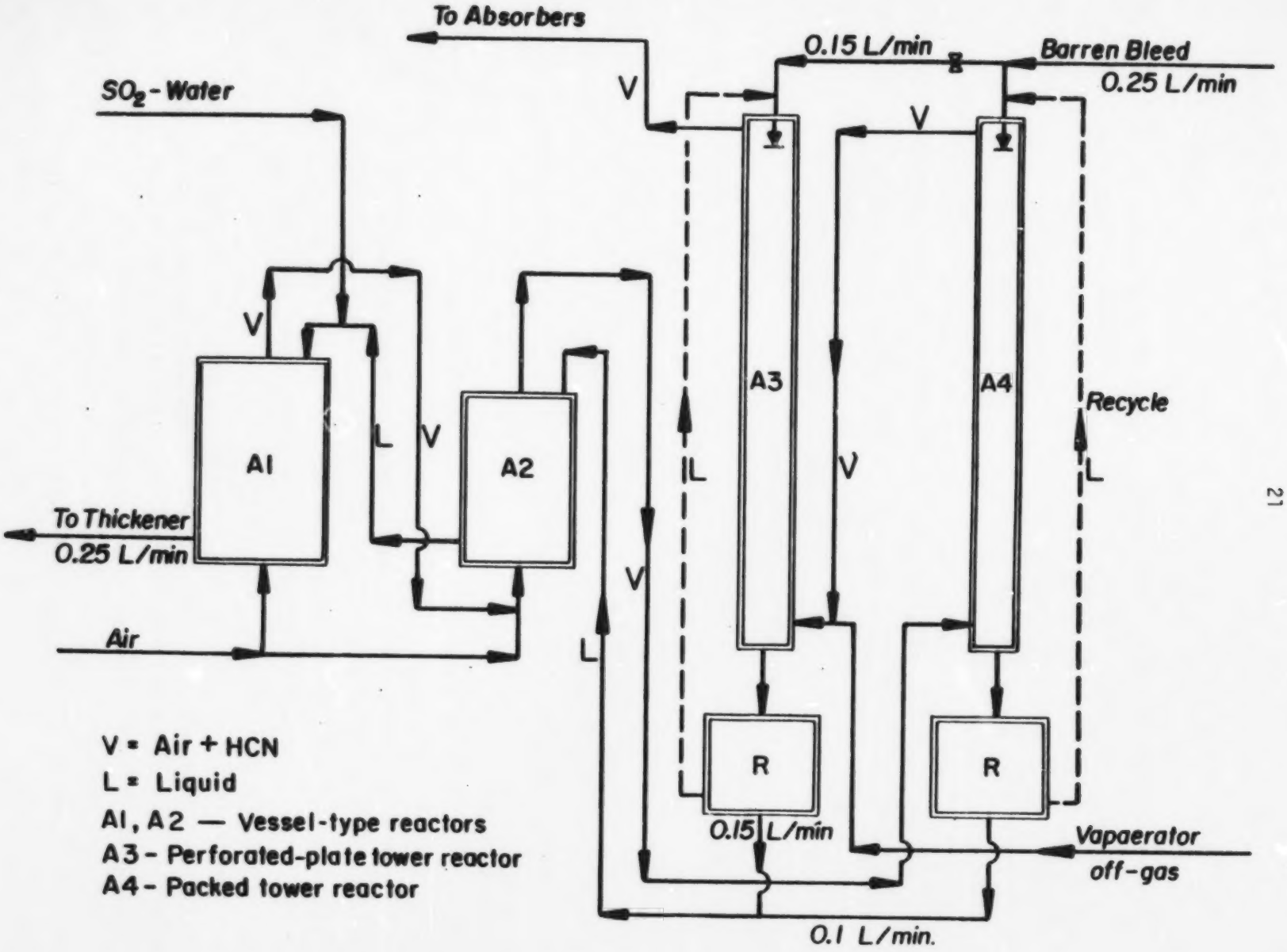


Figure 4 ACIDIFICATION SCHEMATIC: SULFUROUS ACID MODE

gas, may require too many scrub-acidifier units for effective SO_2 utilization. Developments may indicate that a sulphurous acid production route should be a precursor to SO_2 utilization as an acidification reagent.

The input of the SO_2-water required four acidifiers for adequate reagent utilization. In addition to the two vessels used as standard tank-type reactors (A1 and A2), two tower-type reactors were added to function as scrubbers for the SO_2 content in the A1 plus A2 off-gas. Fresh barren bleed, at pH ≈ 11, was the scrubbing medium. If the pH of the solution drops to less than about 8, the SO_2 transport from vapor to liquid is seriously impeded and thus the rapid rates of reaction within the solution are no longer controlling. The solubility of SO_2 in pH 11 solution is high and scrubbing of SO_2 is efficient. To maximize the efficiency of mass transfer the gas scrubbing towers, A3 and A4, contained perforated plates and packing respectively.

The flow system was as follows. The input barren bleed flow was split. At a rate of 0.1 L/min, barren bleed was directed to the top of A4, where it descended through the packed bed and scrubbed the SO_2 from the air which had been used to purge HCN from the contents of reactors A1 and A2. At a rate of 0.15 L/min, barren bleed was directed to A3 where it was utilized to scrub SO_2 from the vapaerator off-gas, along with the A4 off-gas, which still contained some SO_2 due to the SO_2-loading placed upon acidifiers A1 and A2.

Noteworthy are two design considerations. First, in the SO_2 system some absorbed, excess SO_2 still remained in the acidification stage filtrate. This content was purged from solution in the vapaerators and would report to the HCN absorbers if not scrubbed out of the gas stream by fresh barren bleed. Secondly, the HCN content of the combined off-gases from all process reactors is not high (≈0.001-0.002 mole %). This diluted HCN will pass through the SO_2-scrubbing acidifiers (A3 and A4) without affecting adversely the reaction equilibria in solution and thus will not have an affect upon the mass transfer of HCN from the barren bleed to the gas phase. There is no chemical driving force attributable to the HCN content as there is for the SO_2 reactant.

A3 and A4 were installed with liquid recycle from dedicated reservoirs in order to optimize the internal hydraulic flow rates. The pH levels were monitored. If either reactor were to stabilize at an operational pH level

of less than about 8.5, then it would be deemed necessary to add further scrub-acidifier capacity in order to maintain system efficiency.

The liquid exiting the A3 and A4 reactors combined to enter A2, and subsequently A1, where the final pH level was achieved. Acidifiers A1 and A2 yielded a nominal hydraulic residence time of 28 minutes. The staging of pH control over the 4 acidifiers was such that precipitation would occur almost totally in the A1, A2 combination, and slurry stabilization would also occur there. A3 was designed as a perforated plate tower to prevent precipitate build-up on internals when the initial stages of precipitation began at that point in the system. The packed tower, A4, operated as a maximum-efficiency scrubber.

The SO_2-water reagent was pumped to the reactor A1, at an average rate of 6.25 mL/min. It entered with the solution flowing from A2. The hydraulic flow rate was thus increased by 2.5%, an amount which could be neglected here. The air input to A1 was maintained at a rate which was sufficient to ensure stable pH control (pH 2.45) and to cause the purging of unreacted SO_2 gas. The off-gas from A1, carrying SO_2 and HCN components, was injected into A2 as the sparging medium. The A2 off-gas was then scrubbed of its SO_2 content in A4, followed by the A3 pass-through as previously indicated.

This reactor system equilibrated readily when in steady operation. In a full pilot campaign the plant capacity would be established primarily upon vapaerator efficiency and capacity. Therefore it is necessary to incorporate into the system sufficient scrub-acidifier capability to protect the HCN absorbers from sulphate build-up. The requirements must be determined empirically.

The SO2-utilizing AVR process would undoubtedly represent a capital payback proposition if the application was at a minesite where the reagent was available "cost-free". Otherwise sulphuric acid would appear to offer overall cost benefits in so far as acidification reagent choice is decision-controlling.

An SO_2/H_2SO_4 split-control mode also offers a potential advantage. Final stage acidification can be accomplished by H_2SO_4 addition after the initial pH decrease, to pH 5.5 for instance, is accomplished by SO_2. This system enables an appreciable degree of reduction in reagent cost to be realized while eliminating part of the SO_2 overload on the vapour phase.

This mode of operation would result in a lowered requirement for scrub-acidifiers.

II. RESULTS OF ACIDIFICATION/VOLATILIZATION

Table 2 indicates that very little zinco-cyanide was involved in the reactions when H_2SO_4 was the acidification reagent. About 6% precipitated and perhaps an equal amount dissociated. Analyses for total metals (Me_T) were done on the acidified filtrate from sample clarification, which contained both complexed metallo-cyanide anions and simple cations of the metals. The analyses were repeated on the filtrate after neutralization with Na2CO3 to stabilize the cyanide content. The analysis for CN_T was also performed on this filtrate. In this particular sample preparation the metal cations precipitated and the results of analysis indicated the metal content which remains in solution as complex anions (Me_C).

The nickelo-cyanide concentration in solution was lowered to the extent of about 40%; a large proportion of this nickel appears to report, as nickel cyanide, to the precipitate. The results clearly indicate that, although a very satisfactory degree of slurry mixing/purging with air was carried out in the acidifier ($\sim$0.25 m^3 air/m^2/min) there was no appreciable dissociation of even the least stable anionic complexes due to the acidification step alone. Most of the evolved HCN is the result of the reaction of acid with NaCN (or $Ca(CN)_2$).

About 96% of the iron content of the barren bleed was precipitated primarily, if not totally, as a copper-iron cyanide double-complex. The result was that the soluble cuprous cyanide content was lowered by $\sim$95%. The copper to iron ratio in the feed solution was 3.6. The barren bleed supply which was the basis of this investigation contained sufficient copper to enable the precipitation of the stable ferrocyanide species to take place essentially to complete iron rejection from solution (i.e., solution deferrination). The precipitation may have involved $Cu_2(CN)_2$ and/or CuCNS formation as well. A full characterization of the precipitate(s) was beyond the scope of the present work.

The acid consumption was 0.91 kg H_2SO_4 per metric tonne of barren bleed.

Table 2. Solution Analysis (mg/L); H_2SO_4 Acidification Mode; Steady State Operation

(H.F.R. = 0.4 L/min)*

	Total Metal (Me_T)				"Complexed" Metal+ (Me_C)				CN_T
	Zn	Cu	Ni	Fe	Zn	Cu	Ni	Fe	
Barren Bleed	50	65	40	18	-	-	-	-	375
Acidifier 1 RT = 10 min; pH = 2.5	49	6	34	0.1	47	6	30	0.3	226
Acidifier 2 RT = 7 min; pH = 2.5	48	7	34	0.2	46	7	30	0.3	216
Thickener 1 (RT = 10 min)	44	7	29	0.2	42	7	27	0.2	214
Thickener 2 (RT = 90 min)	47	6	26	0.1	44	5	23	0.4	180
Clarifier reservoir (post-filtration)	47	3.8	24	0.3	44	3.4	22	0.4	128
Vapaerator RT (min)									
19	-	-	-	-	31	3.3	21	0.6	60
38	-	-	-	-	0.1	3.2	20	0.1	33
57	-	-	-	-	0.1	2.7	11	<0.1	22
76	-	-	-	-	0.2	2.4	7	<0.1	12
95	-	-	-	-	0.2	2.1	3	0.1	5.3
114	-	-	-	-	0.1	1.8	1.4	0.1	2.5
174	-	-	-	-	0.2	1.7	0.3	<0.1	<0.2
234	-	-	-	-	0.3	1.5	0.2	<0.1	<0.2

*H.F.R. = hydraulic flow rate

+Me_C = metal content of neutralized (pH = 10) and clarified samples

The gelatinous, slow-filtering precipitate produced an "acid-cake" which reported as 74% moisture. The dried acid-cake (at 75°C) amounted to 0.26 kg/tonne of barren bleed.

Table 3 shows the extent of the changes in precipitate slurry equilibrium, with pH, when SO_2 was the precipitating reagent. In this experiment about 28% of the zinc was already precipitated as the cyanide at pH 7.7. At this point much of the ferrocyanide had also precipitated, probably as the complex zinc ferrocyanide. However, a portion of the iron appears to have been freed as a cation due, perhaps, to partial dissociation of an iron-complex component in the barren bleed. The cationic iron apparently recombined with cuprocyanide anions at a lower pH level to yield neutral salt. Approximately 37% of the cupro-cyanide anion content had been influenced at pH 7.7, with reactions seemingly yielding both precipitated species (~10%) and cations (~27%). The latter were also complexed to form neutral salt under increasing acidity. With SO_2 input for acidification, the $Ni(CN)_4^{=}$ is the component which is only slightly dissociated (~10%), even at pH 2.45. Very little precipitation of neutral nickel cyanide occurred.

The drop in pH from 7.7 to 2.45 in acidifier A1 results in most of the cupro-cyanide complexing into a solid form which would appear to include both copper-iron species and CuCNS. The final precipitate mixture was substantially lighter in color (yellow-brown) than the dark reddish-brown observed for H_2SO_4-induced precipitation.

The SO_2 consumption was 2.09 kg per metric tonne of barren bleed.

The gelatinous precipitate produced an acid-cake which reported as 56% moisture. The dried acid-cake (75°C) amounted to 0.27 kg/tonne of barren bleed.

There were, obviously, several substantial differences in the acidification circuit control for H_2SO_4 addition versus SO_2-water addition (eg. overall hydraulic R.T., air sparging methodology and pH profiling). However, the precipitation-stage net results are not too dissimilar. Sulphuric acid caused considerably less zinc cyanide precipitation but resulted in more nickel cyanide being rejected into the precipitate. Although precipitated species are undoubtedly quite different, the degree of net rejection of iron and copper content from solution was about the

Table 3. Solution Analysis (mg/L); SO2-Water Acidification Mode; Steady State Operation

(H.F.R. = 0.25 L/min)*

	pH	Total Metal (Me_T)				"Complexed" Metal+ (Me_C)				CN_T	CNS
		Zn	Cu	Ni	Fe	Zn	Cu	Ni	Fe		
Barren Bleed	11.1	50	65	40	18	-	-	-	-	375	290
Scrub-Acidifier A4 (RT = 8 min)	9.0	49	64	41	17	48	48	37	11	324	295
Scrub-Acidifier A3 (RT = 4 min)	8.3	46	59	40	15	46	49	35	6.5	316	280
Acidifier A2 (RT = 12 min)	7.7	36	59	40	8	34	41	36	5.2	279	290
Acidifier A1 (RT = 16 min)	2.45	22	0.5	40	0.5	21	2.6	34	0.7	240	230
Thickener	2.45	-	-	-	-	-	-	-	-	-	-
Clarifier reservoir (filtrate)	-	21	2.1	39	1.0	20	3.8	35	0.9	184	230
Vapaerator RT (min)											
31	2.47	-	-	-	-	0.1	2.0	30	0.1	50	-
62	-	-	-	-	-	0.1	1.9	13	0.1	24	-
93	-	-	-	-	-	0.1	1.4	5	0.1	8	-
124	-	-	-	-	-	0.1	1.3	0.8	<0.1	1.3	-
194	2.47	-	-	-	-	0.1	0.9	0.2	<0.1	<0.2	-
264	2.47	-	-	-	-	0.1	1.0	0.2	<0.1	<0.2	-

*H.F.R. = Overall hydraulic flow rate

+Me_C = metal content of neutralized (pH = 10) and clarified samples

same. This ensured that ferrocyanide was not a problem area for event l waste water specification attainment.

At pH≈2.5, where the concentrations of copper and iron are very l , some apparent anomalies are indicated. Me_C reports greater than Me_T . It is possible that minute quantities of ferrocyanide and/or cuprous cyanide anionic complexes migrate to the walls of the sample container under acidic conditions. Me_T would report too low. When samples are adjusted to pH≈10, complex anions would be totally in solution. Since there is very limited dissociation of soluble complexes during acidification, the effect of copper and iron cations upon metal concentrations is negligible.

Overall, the cyanide (CN_T) content of the filtrate from acidified and clarified barren bleed ranged from one third of the head value (H_2S mode) to one half the head value (SO_2-water mode). The actual proport ons of CN_T which are precipitated or, alternatively, released by evolution f HCN is not a concern when evaluating AVR application to any particular old mill barren bleed. It is important to fully appreciate the extent to w ich precipitation of stable cyanide species will take place. It is also significant that the positive air agitation/purging applied to acidifie s A1 and A2 did not efficiently evolve the available HCN. The combinatio of residence time in the thickeners, plus the filtration step, caused a considerable drop in the [CN_T] in the solutions, as is evident from the data shown in Tables 2 and 3. In the laboratory, those operations were open to atmosphere. In a larger scale campaign the units should be enclosed and vented to the absorber headers.

An obvious conclusion relates to the significant solubility of HCN n aqueous solutions, even when the acidity level is appreciable. The effective evolution of molecular HCN from acidified barren bleed requir s either a prolonged residence time in moderately-agitated, vented vessel or intensive gas phase stripping in reactors. Only the latter method can e realized as being efficient and therefore acceptable as a processing parameter.

The solution flow rate for the H_2SO_4 experiment was such that a lo g residence time was required in the #2 thickener (1.5 h). Furthermore, ie residence time in the acidifiers was 17 minutes, compared to 40 minutes for the SO_2-water system. Copper/nickel precipitation reactions continued, n

the H_2SO_4 run, onward into the solid/liquid separation stage. This would indicate that some important precipitation reactions have an appreciable time-dependency. The hydraulic residence time in the acidification step should not be unnecessarily restricted. Interaction of precipitating complex species, with time, could be of significance to process efficiency, especially in respect to Cu, Ni and Fe cyanide anionic species which reside in a solution in which the released cyanide ion is continuously being depleted by protonation and subsequent evolution.

III. VOLATILIZATION

Clarified solution at pH = 2.5 entered a cylindrical steel vessel (designated as a vapaerator) through a port located near the bottom. Air input was via the same port. The vessel was 22 cm in diameter and 25.4 cm deep, inside measurements. A high speed (1750 rpm) impeller ensured that maximum dispersion of air throughout the bulk solution (7.7 L) was achieved. Volume expansion was accommodated by use of an auxiliary aeration tower. The off-gas was directed to an HCN absorber system when the acidification was in the H_2SO_4 mode; to acidifier A3 when in the SO_2-water acidification mode.

Air is utilized as an HCN-stripper in the AVR process. Oxidation of CN^- (to CNO^-) is <u>not</u> involved. If oxidation has any function it is very limited and would only involve the cuprous-cupric ionic relationship.

Only one vapaerator was installed (refer to Figure 3). Therefore increments of hydraulic retention time were accumulated by pumping a collected volume of single-pass effluent through successive stages of vapaeration until the [CNT] reported at about 0.2 mg/L. Pumping rate equalled the selected hydraulic flow rate for the run.

When the H_2SO_4-acidified water was aerated, the air input volume rate was 125 times the acidified solution volume flow rate (50 L/min air vs 0.4 L/min water). In the case of the SO_2-water mode the air input rate was 220 times the solution flow rate (55 L/min air vs 0.25 L/min water). The hydraulic residence times were 19 min and 31 min, respectively, per reactor pass.

Air per unit of reactor cross-sectional area was almost equivalent (for H_2SO_4 mode 1.32 $m^3/m^2/min$; for SO_2-water mode 1.46 $m^3/m^2/min$). The

latter relationship is the one that relates to the provision of the driving force for efficient dissociation of metallocyanide anionic species, assuming that gas bubble dispersion efficiency is a constant (refer to discussion of volatilization of HCN on page 10). A factor in the experimental assembly which cannot be quantified is the effect of the high speed vane rotator. It was the means for ensuring bubble dispersion in the present work. Because mechanical features of this type are not suitable for scale-up, a pilot plant vapaerator design would involve some type of static multiple-orifice distributor, of the same cross-sectional area as the vapaerator tank.

The results shown in Tables 2 and 3 clearly indicate that the two acidification reagents are equally effective from a chemical point of view. The hydraulic residence time in the vapaerator required to yield virtually complete dissociation of $Ni(CN)_4^{=}$ is equivalent for the two acidification modes.

Cupro-cyanide anionic species exhibit very high stability in dilute acid; they undergo extremely complex chemical reactions in gold milling solutions; and they may result in microparticulate formation under intense aeration. In the present work there is evidence that a minimal amount, approximately 1 mg/L on copper metal basis, could report to the final effluent. However, the intensity of aeration was substantially less in this test assembly than that level which would be designed into a pilot-plant facility. In a pilot-plant design the vapaerator pneumatic flow rate should be at least 5 $m^3/m^2/min$, and the air to liquid volume flow ratio a least 250/1. Improved design would be expected to enhance all aspects in regard to the efficiency of dissociation of the very stable anionic complexes.

It is not known why the analytical feedback consistently indicated negligible CN_T content in the vapaerator effluent when the total metal content reported at 1 to 2 mg/L. Samples were always reneutralized and clarified, thus removing metal cations. As will be shown later, the final AVR effluent from the two runs contained the cyanide component in approximately stoichiometric amount in regard to traces of metal content.

It is specially noted that samples of acidified barren bleed, from all processing stages, were neutralized with Na_2CO_3 primarily to stabilize the

cyanide content. There has been no suggestion that this sample treatment would interfere with the cyanide determination in the 1 part per million range.

IV. RENEUTRALIZATION

Vapaerator final effluent flowed directly to the neutralizer vessel where control was by milk of lime addition to pH 9.5. The retention time was approximately 10 minutes. The slurry outflow went to a centre-well thickener, where there was 1 to 1.5 hours residence time depending upon flow rates. The thickener overflow was clarified and analyzed as final AVR waste water. The results are shown in Table 4. The underflow was filtered and the "neutral cake" was stored for subsequent treatment in the nickel and zinc recovery step.

If the reneutralization slurry was pumped to a tailings pond in practice, then the contained metal hydroxides would readily resolubilize when natural factors lowered the pH of the water. This could adversely affect pond overflow specifications.

The precipitate content of the slurry amounts to approximately 0.3 kg/tonne barren bleed treated. The precise quantity is dependent upon the barren bleed characterization, the acidification agent used, the operating pH level in the treatment system, and the final pH of neutralization.

Based upon analysis of precipitate produced from the present study, the quantity of nickel, for example, recoverable from the "neutral-cake" via a simple, small-scale leaching operation is shown in Table 5. In the H_2SO_4 acidification mode zinc recoverable from the neutral-cake amounts to 17.3 tonnes per year. The copper reports almost totally to the "acid-cake" at 23 tonnes per year.

Table 4. Analysis of Process Waste Water Discharge (mg/L)

Component	Acidification Reagent	
	H_2SO_4	SO_2-water
CN_T	1.0	2.0
Zn	<0.1	<0.1
Cu	0.7	0.9
Ni	0.1	1.4
Fe	<0.1	<0.1
CNS	160	185
CNO	5.3	5.4*
Co	0.1	0.4
Au	0.07	0.06
As	0.02	0.16

*Note that utilization of sulfurous acid as a reagent did not result in oxidation of CN^- to CNO^-

Table 5. Nickel Recoverable as a Mixed-Metal Concentrate from the Neutral Cake (per year)

(365 days @ 1000 tonne barren bleed processed per day)

Acidification Reagent	Precipitate (Neutral Cake)		
	tonne/a (dry basis)	Nickel	
		(%)	(tonne/a)
H_2SO_4	109.5	9.5	10.4
SO_2	73	18.7	13.6

The complete operational flowsheet for the integrated treatment of precipitates will be the basis for a subsequent paper. Full environmental accountability can be achieved at relatively small additional cost.

Hydrated lime was used to adjust the aerated water to the required level for metal cation precipitation. In both operational modes the pH of the vapaerator output solution was higher than the pH level of the acidifier filtrate.

The lime was milled to a very fine but unquantified particle size, as an aqueous slurry, in order to maximize reneutralization efficiency. Retention time in the reneutralizer should be as long as is practical, agitation as vigorous as possible, and the milk of lime feed rate consistent.

Table 6 shows the reneutralization data for the two optional treatment schedules. The pH values, at this end-of-process adjustment step, are somewhat flexible. In regard to the pH rise observed during aeration, it may be preferable to inject just enough acid into the vapaerator feed to maintain pH at the acidifier output level (2.45 to 2.5).

Table 6. Reneutralization Unit Operation

	pH		Hydrated Lime Requirement (kg/tonne)	Precipitate Metal Content* (%)
	Input	Output		
H_2SO_4	2.65	9.2	0.487	26.4
SO_2-water	2.80	9.1	0.420	29.4

*Ni + Zn + Cu + Fe

V. ANALYSIS

All analyses for CN_T were done by the distillation technique (ASTM Standards, Method A) (14). For liquid head samples (pH ≈ 11) all of the cyanide associated with the iron content will report. This represented about 50 mg CN/L. However iron is rejected from solution at the acidification step, so ferrocyanide is not a factor in the overall AVR process if the deferrination of the solution is complete, as is usually the case.

The metals of interest are reported from atomic absorption methodology. If ferrocyanide is present in solution, the iron content indicates the extent if the sample pH is adjusted to ≈10 and then clarified.

Essentially the same analytical methods were used for analysis of precipitates. For solids, however, the analytical result for $[CN_T]$ may not reflect quite all of the cyanide present as the double complex(es) of copper, zinc and iron cyanides. The analytical distillation step will not necessarily dissociate such species to completion. The technique is less rigorous than the process precipitate treatment procedures.

The following table shows the lower detection limit of the analytical methods applied to this project.

CN tot	0.1 ppm	CNO	0.01 ppm
Zn	0.1 ppm	Co	0.1 ppm
Cu	0.1 ppm	Au	0.01 ppm
Fe tot	0.1 ppm	As	0.01 ppm
Ni	0.1 ppm	S tot	1.0 ppm
CNS	1.0 ppm	SO_4	0.01 g/L

Stabilization of all liquid samples, other than heads, which were submitted for analysis of total cyanide was achieved by neutralization with Na_2CO_3. This step was taken as soon as possible after the sample was withdrawn from the circuit and filtered.

Neutralization of clarified solutions often resulted in precipitate formation. The precipitate consisted principally of a mixture of zinc, nickel and copper hydroxides. The amount of precipitate reflected the

degree of dissociation of the metallocyanides. The acidified, moderately-aerated solutions (eg., acidifier samples) produced very little or no precipitate upon neutralization with Na_2CO_3. As the acidified solution progressed through successive stages of vigorous aeration (vapaerator samples) the precipitate became more voluminous and the green colouration of $Ni(OH)_2$ became more noticeable. Complexed metal (Me_C) is taken to be the soluble metal content of clarified solution at pH ≈ 10.

The analytical work for this study was contracted out to the analytical firm Bondar-Clegg and Company Ltd. of Ottawa, Ontario. Campbell Red Lake Mines Ltd. covered the cost of the contracted work.

ECONOMIC CONSIDERATIONS

In general, when recovery of cyanide from waste solutions such as gold mill barren bleed is referred to in the literature, allusions are made in regard to slow reaction rates for dissociation and to the toxicity of HCN gas. It appears necessary to substantially sharpen the focus upon the very real advantages of the AVR process.

The process uses unsophisticated technology. Process control is by simple pH-actuated flow controllers applied to acidifier and reneutralizer unit operations. All slurries involved in the process staging are very low density. Control mechanism and operational parameters are essentially independent of contaminant concentrations in the barren bleed and are therefore normally independent of milling and leaching circuit operation. In certain unique situations an added dosage of metal cations might be required in order to optimize acidifier precipitate formation. However, if required, the Cu^{2+}/Zn^{2+} and/or Fe^{2+}/Fe^{3+} cations are recyclable, from a novel precipitate treatment step, in order to ensure the optimized precipitation of copper ferrocyanide complex(es).

Figure 5 (see Appendix 1) is a flowsheet which has been developed to indicate the equipment requirements as presently projected (i.e., no inclusion of pretreatment or post-treatment process enhancement technology) to treat 1000 metric tonnes per day of barren bleed having an average total cyanide content of 500 mg/L (analyzed as CN_T). The cyanide content, whether complexed strongly or weakly or uncomplexed (i.e., "free"), can vary up to 100 mg/L, or more, without a significant effect on

process requirements. The higher the CN_T content, the more economically viable the process. Fresh barren filtrate, containing the maximum amount of uncomplexed cyanide, represents a most attractive feed for AVR since this portion of the reusable reagent is recoverable with ease.

I. CYANIDE FOR REUSE

If the strong acid/distillation step for the acidification-induced precipitate is installed, as indeed it should be, then the CN_T content of the barren bleed represents the recoverable cyanide (as HCN). The CN_T, as determined by Method A in the ASTM Standards (14), includes the cyanide associated with the iron content of the barren bleed.

The potential recovery of cyanide, at CN_T = 500 mg/L, will convert to about 940 kg/day NaCN upon absorption of the HCN by NaOH. At a current market value of $2.00 per kg NaCN, the daily processing return via reagent saving would be approximately $1,880. If we assume that an overall 10% cyanide loss may be unavoidable, then the net value of recovered reagent would be the order of $1,700 per day or $620,000 per year.

The total process cost, per day, for H_2SO_4, NaOH, $Ca(OH)_2$, polyelectrolyte and electric power (for vapaeration) was calculated at $1,200.

The HCN absorption step can be equally effective when using milk of lime as the absorbing medium.

II. UNSTABLE METAL HYDROXIDES: ENVIRONMENTAL ASPECT ACCOUNTABILITY

The precipitates formed in the acidifier, termed the "acid-cake" when filtered off, are specifically scheduled for a small-scale cyanide recovery step. In the present application these precipitates, which are to be treated with hot concentrated H_2SO_4, amount to 260 kg/day (dry weight). Copper, nickel and zinc content is ~30% and the cyanide content (CN_T) is ~20%. The iron, which is ~7% by weight of dry precipitate is rejected as a cyanide-free, stabilized precipitate when the acid-cake is digested. This treatment results in a concentrated solution of the non-ferrous metals. Any required portion of this copper-rich sulphate solution may be recycled to the equalizor tank for blending with the barren bleed. Finally, the metals in solution are converted to an oxide form, by precipitation of

mixed hydroxides, for easy storage. The filtrate is, in part, recyclable to acid-cake digestion as reagent and water make-up.

The reneutralization precipitate ("neutral-cake", when filtered off) analyzed 25% combined nickel and zinc. Relatively little copper reports here. The precipitate quantity would be ~300 kg/day. A small scale, dilute acid leach removes the metal values from the principal waste component, gypsum. The leach solution is combined with the "acid-cake" leach solution for the iron-elimination step and subsequent concentrate preparation.

The overall concentrate of Cu-Ni-Zn oxide can be readily shipped, periodically, to a metal processor. No toxic metal components of the original bleed are directed to the tailings pond from which they would eventually report into the watershed. Furthermore, no toxic components which can report to the final effluent are added to the bleed during the AVR treatment procedures.

The iron-free Cu-Ni-Zn concentrate, as metal oxides, amounts to ~200 kg/day or 73 tonnes per year. The current nominal market value of the contained metal is $125,000 per year. Any reasonable percentage recoverable should offset the operating cost of precipitate treatment. The potential cyanide recovery from the acid-cake is 60 kg/day, or 113 kg NaCN/day. This represents $200/day credit to precipitate treatment (at 10% processing loss) or about 12% of the total NaCN reusable, based upon the barren bleed component parameters chosen for the calculations.

Therefore, in summary, by fine-tuning the focus on the AVR cyanide recovery process, one can see that a substantial payback on capital or operating costs can be achieved and the benefits to the environment are such that no future problem(s) will accrue.

Table 7 shows the total quantities of copper, nickel and zinc which report to the two precipitates, for the H_2SO_4 acidification mode. Also shown is the distribution of the metals which is the result of the processing stages. The iron reported ~96% to the acid-cake. The remaining ~4% reported to the neutral-cake. There was no iron content in the final waste water. The treatment of precipitates provides for discard of the iron component. Per cent distribution is based upon analysis of precipitates.

Table 7. Metal Content of Barren Bleed Reclaimable from Process Precipitates

(Basis: 1000 tonne barren bleed/day)
Acidification Mode: H_2SO_4

Metal	Conc. in bleed (mg/L)	Quantity Recoverable		Distribution %	
		per day (kg)	per year (tonne)	Acid-cake 260 kg/day (dry)	Neutral-cake 300 kg/day (dry)
Cu	65	65	23.7	97.1	2.9
Ni	40	40	14.6	29.1	70.9
Zn	50	50	18.3	5.6	94.4
Fe	18	Discard	Discard	95.8	4.2

The distribution of the metals to the two filter cakes, for the SO_2-water acidification mode, is shown in Table 8. The results are based upon precipitate analysis, and on 1000 tonnes per day barren bleed processed.

Table 8. Per cent Distribution of Metals in Precipitates

Acidification Mode: SO2-water

Precipitate	kg/day (dry)	Cu	Ni	Zn	Fe
Acid-cake	270	98.0	6.7	61.7	94.4
Neutral-cake	200	2.0	93.3	38.3	5.6

III. PROCESS EQUIPMENT DISCUSSION

Figure 5 can be viewed as a first approximation to a full-scale operation (1.137 m^3/min; 250 IGpm). This conceptual interpretation is based upon experience gained from extensive laboratory testing and also

upon an examination of the literature relating to processing of complex cyanide-containing solutions. The layout does not preempt the requirement for a pilot-plant campaign at a minesite. Furthermore, it is not intended to represent an exclusion of other reactor design or tankage capacity which may be more amenable to the restrictions placed upon a mill superintendent or process consultant.

A one-operating-day supply of barren bleed (~15 h @ 250 IGpm) is resident in two 500 m^3 (110,000 IG) equalizor tanks. Although acidification control is independent of barren bleed content, this capacity may be required if there developed a need for recycle of Cu^{++}/Zn^{++} to ensure that the ferrocyanide is rejected into the precipitate upon acidification. If such addition was advantageous, then analysis of pre- and post-dosage barren bleed metal content would be required for chemical control. The acidifier feed would be blended so as to allow deferrination of the solution to proceed during acidification.

Although not investigated in the current study it may also be feasible to lower substantially the $Cu(CN)_3^=$ content of the barren bleed by chemical equalization of the two most stable anionic complexes, ferrocyanide and cuprocyanide, in regard to the stoichiometric requirements for the precipitated double complex, copper ferrocyanide.

The flow sheet indicates optional dosage locations. In an extended pilot study this hypothetical controlled-complexation feature should be investigated concurrently. The potential advantages of this concept, if investigated prior to finalizing process design are: (1) The "dissociation-load" on the vapaerators might be lowered by increasing copper cyanide precipitation in the acidifiers. Cupro-cyanide is the most stable soluble component in the acidified barren bleed. (2) The most appropriate dosing system could be established for the particular mode of control that may be required, i.e., guaranteed precipitation of $Fe(CN)_6^{4-}$ in total by Cu^{++}/Zn^{++} addition or, alternatively, precipitation of excessive copper cyanide content by complexation with added ferrous or ferric iron.

The precipitation mechanism has not been clearly defined. Therefore the optimum pH level for application of equalization techniques is not presently suggested. Cyanide ion (CN^-) could be directly involved in the reactions, even if only transiently present in the solution.

The use of H_2SO_4 as an acidification agent should involve 2 acidifier reactors in series to minimize short-circuiting of solution and to maximize chemical stabilization of the slurry. Twenty minutes retention time per acidifier would enable thorough aeration of the slurry in order to achieve an adequate evolution of the HCN formed by the many reactions occurring simultaneously. Most of the molecular HCN should be evolved prior to thickener entry. This would minimize cyanide losses.

To optimize precipitate coagulation, a flocculator is installed which has a residence time of ~10 min. Polyelectrolyte solution (0.05 g polymer/L water) is added at an optimized dosing rate. Mixing must be gentle in order to facilitate floc formation. The slurry proceeds to the deep-well thickener #1, yielding to a nominal residence time of 2.8 hours, based upon designed hydraulic flow rate. Thickener #1 overflow moves by gravity to thickener #2 where the residence time is 1.4 hours and "rapid-settling" enhancers are added. Thickener #1 underflow is, in part, recycled to the unit entry box in order to promote densification of the precipitate sludge. The portion not recycled is pumped at suitable intervals to the sludge reservoir. Thickener #2 overflow is pumped through clarifiers (sand and/or multimedia) as required. The requirement is freedom from fine particulate matter which represents precipitated metallo-cyanide complexes and gypsum. Thickener #2 underflow is returned to the #1 thickener feed box (pre-entry blender).

The thickeners are equipped with covers and the internal free board space is flushed with air which is directed to the HCN absorber header system.

Efficiently clarified solution is passed through the vapaerator units (three) in counter-current flow to the HCN-stripping airflow. The HCN-laden air goes to the caustic (or lime) absorption towers and is then vented. The solution, in which the metal content is present primarily as simple cations, flows to the reneutralizer where metal hydroxides and gypsum are precipitated by addition of milk of lime.

In a minimum-sensitivity aquasphere region the reneutralizer outflow could be directed to ponding. In a more sensitive region the unstabilized and potentially toxic precipitate would be readily and advantageously detoxified by a procedure which is indicated in the flowsheet. The metal content of the "neutral" precipitate is recoverable.

The absorber units are intended to accommodate all HCN-laden air streams. Counter-current flow of caustic solution and air will enable maximum practical utilization of absorber capacity. The absorption columns are operated with sub-flooding conditions of caustic recycle from dedicated reservoirs. They can be packed columns for caustic absorbant or perforated plate columns for operation with milk of lime. An empirical evaluation of capacity lead to the scale-up shown in the flowsheet, which is expected to be conservative. The chemical reaction involved is fast. Absorber Ab-3 is, in essence, a scrubber which would serve to remove caustic entrainment from the air stream.

Metals recovery from precipitates has been indicated on the flowsheet where appropriate. Novel procedures developed for this integrated processing step are the subject of a separate report.

When a pilot-plant campaign is developed at, for example, 0.1 scale (0.114 m^3/min or 25 IGpm) then the operating parameters suggested in this study can be assessed by utilization of readily modifiable equipment which would simulate or approximate design features which have been discussed.

IV. VAPAERATOR DESIGN: CONCEPTUAL

It has been established that all unit operations comprising the AVR process are standard except one. The vapaerators must generate sufficient mass transfer driving force to enable the HCN solute to instantaneously, upon formation, transfer from the bulk liquid to the gas phase. As previously discussed, the liquid phase is controlling due to the solubility of the solute in the liquid and the extremely limited HCN concentration gradient. Chemical equilibrium constants are so low for metallo-cyanide anionic complexes in weak acid solution, particularly for $Cu(CN)_3^{=}$ and $Ni(CN)_4^{=}$, that the dissociation reaction product concentration ($[CN^-]$) must approach zero at all times.

In the laboratory experiments the key operating parameters for the vapaerator, when under maximum load conditions were:

i) the hydraulic retention time range was 20-30 minutes.

ii) the airflow rate per unit of reactor area was $\approx$1.72 $m^3/m^2/min$ (5.64 $ft^3/ft^2/min$).

iii) ratio of total air input rate (L/min) to total liquid input rate (L/min) was variable within the range 125-220.

iv) bubble size and dispersion efficiency were established by a high speed, vaned rotator. This factor was not variable.

The results and observations which accrued from the test work enabled specifications to be formulated for scale-up purposes. It is assumed that an air disperser grid placed at the bottom of each aeration tank would best apply to an industrial unit. The air bubbles must be distributed evenly over the total reactor area. The number of orifices should be maximized and the orifice diameter minimized to yield a dispersion of very fine bubbles.

Multiple vapaerator units are required, operating in series, with clarified acid filtrate moving counter-current to air flow direction. If the static liquid height in a vapaerator unit is too high then bubble coalescence may occur when the unit is operational. This effect would seriously decrease the efficiency of the HCN-stripping. Obviously the opportunity for hydraulic short-circuiting must be minimized. This also requires series operation of vapaerators, possibly involving a baffle arrangement within each unit.

The following specifications were submitted to the Office of Technology Transfer (OTT), CANMET, along with a request for a capital equipment, plus energy cost, estimate for the aeration-volatilization stage of the AVR process:

i) three reactors in series, with counter-current air and solution flow.

ii) solution hold-up time per reactor @ 42 min.

iii) airflow rate per unit area = 4 times the laboratory test rate, or 6.86 $m^3/m^2/min$. (22.5 $ft^3/ft^2/min$).

iv) static height of solution 1.22 m (4 ft).

v) acidified solution feed rate @ 1.137 m^3/min (250 IGpm).

The above parameters assured that the volume flow ratio was 236/1 (m^3 air/min to m^3 liquid/min).

F.J. Kelly, Project Analyst, performed the following detailed calculations for equipment design and capital cost (15).

Metric conversion factors: 1 m = 3.28084 ft

$1\ m^3$ = 219.97 Imp. Gal.

1 atm. = 101.3 kPa

1) Reactor:

Volume = flow x holdup

= 1.13652 x 42

= $47.73\ m^3$

Area = vol/static water height

= 47.73/1.2192

= $39.15\ m^2$

Diameter $= \sqrt{\frac{4 \times \text{area}}{3.14159}}$

$= \sqrt{\frac{4 \times 39.15}{3.14159}}$

= 7.06 m = 23.16 ft

2) System pressure drop

Estimated losses:

sparger	1.245 kPa
static water	11.950 kPa
pipe 12.192 m	0.200 kPa
pipe 6.095 m	0.100 kPa
baffle	0.249 kPa

		kPa
Reactor - 3	baffle	0.249
	static water	11.950
	sparger	1.245
	∠ R-3	13.444
Reactor - 2	piping	0.200
	baffle	0.249
	static water	11.950
	sparger	1.245
	∠ R-2 + R-3	27.088

Reactor - 1	piping	0.200
	baffle	0.249
	static water	11.950
	sparger	1.245
	piping	0.100
	Σ R-1 + R-2 + R-3	40.832

3) Air displacement volume

Estimated bubble rise time for 6.35 mm dia. bubbles = 0.25 m/sec

Air rise time = static water height/bubble rise time

= 1.2192/0.25

= 4.88 sec

Displaced air vol height = air flowrate ($m^3/m^2/sec$) x air rise time

$$= \frac{6.858}{60} \times 4.88$$

= 0.56 m say 0.65 m

Reactor height = static water height + displaced air vol height + sparger height + water disengagement height

= 1.22 + 0.65 + 0.31 + 0.87

= 3.05 m = 10.0 ft

4) Compressed air requirement

Airflow = reactor area x airflow rate ($m^3/m^2/min$)

= 39.15 x 6.858

= 268.5 m^3/min

say 320 m^3/min at 55.2 kPa at 20% safety factor

Airflow at 689.2 KPa

$$\text{Vol} = \frac{(55.2 + 101.3)\ 320}{(689.2 + 101.3)}$$

= 63.3 m^3/min at 689.2 kPa

Capital Cost Estimate

Qty	Item	$
	Air compressor 63.3 m^3/min at 689.2 kPa	191300.
1	Air receiver steel 9.5 m^3, 689.2 kPa	6000.
1	Cooling water pump & motor 0.38 m^3/min	1350.
3	Reactors steel, 7.06 m Ø x 3.05, 345 kPa	80000.
2	Solution pump & motor 1.14 m^3/min	4250.
	Main equipment	283170.
	Freight, sales tax, miscellaneous (18% of main equip.)	50970.
	Delivered equipment	334140.
	Field material 10% of delivered equipment	33410.
	Installation 33% of delivered equipment	110270.
	Installed equipment	477820.
	Piping, 20% of installed equipment	95560.
	Electrical, 20% of installed equipment	95560.
	Instrumentation, 5% of installed equipment	23890.
	Total Direct	692830.
	Contingency, 10% of total direct	69280.
	Fixed Capital	762110.
	say	$763000.

The above estimate does not include any allowance for building, engineering, construction management and contractor's fee. Power requirements are: compressor 298.3 kw, cooling water pump 2.3 kw and solution pumps 3.8 kw each for a total of ~310 kw. If electricity costs $0.0352/kwh the operating cost is $0.16/$m^3$ of barren solution treated.

Vapaerators designed according to the above specifications demand a considerable floor area. If adapted to stack vertically, the three-unit vapaerator would be compact. The total liquid content of the three units is 143 tonnes (31,550 IG).

AN AVR-REVERSE OSMOSIS INTEGRATED CIRCUIT

The application of AVR technology to the treatment of major quantities of dilute waste water, which gold mill barren bleed represents, has lead to the development of a unique concept. It is proposed that reverse osmosis technology (RO) be applied to the barren bleed or, alternatively, to a suitable stage of cyanide recovery, in order that the content of the solution may be concentrated several fold. This would be particularly effective in regard to the metallo-cyanide soluble complexes. They would be more efficiently dissociated in the vapaerators if the unit process input concentrations were considerably higher. Simple laboratory tests have indicated that the acidified and filtered barren bleed (pH ≈ 2.5) can be reduced in volume by a factor of ≈8 without further precipitation or "salting out" of the components. Recent advances in membrane technology have led to the development of materials which can perform well across the pH range from 2 to 11.

Laboratory experiments with natural barren bleed (pH ≈ 11) preconcentration has indicated that a degree of precipitation may result within a limited pH range. There is also the consideration of the greater complexity of components than is the case involving acidified and clarified bleed. However, if reverse osmosis was amenable to treatment of barren bleed directly then further capital cost saving and increased efficiencies would be realized in the overall cyanide recovery process.

Following is a generalized conception applying to certain individual steps in the AVR process which would be affected by RO application. It will be seen that there are, potentially, substantial advantages to be gained by AVR integration with reverse osmosis. Assume a conservative concentration factor of 5:1 for reverse osmosis. Furthermore, assume that this application would be equivalent in capital costs to those normally pertaining to the desalination of brackish water.

1) Reverse osmosis (RO) applied to acidified barren bleed

   a) aeration-volatilization stage

      AVR Vapaerator capital cost (incl. installation) $763,000
      @ 1000 tonnes/day

      Electrical energy (compressor) $160/day

AVR + RO

Vapaerator capital cost @ 200 tonnes/day
(assume, conservatively, that only 60% reduction
is realized)

$763,000 x 0.4 = $305,000

RO capital cost @ $1/U.S.gal/day (installed) = 264,000

Total $569,000

Electrical energy (compressor)

$160 x 0.4 = $64/day

b) reneutralization stage

slurry volume, and therefore thickener size,
reduced by ~80% due to RO

c) final effluent

AVR 1000 tonnes/day to pond

AVR + RO 800 tonnes/day quality water (permeate): plant reuse.
200 tonnes/day discard to pond: contains same total
amount of CNS^- and thiosalts. However, the high CNS^-
concentration may make the solution amenable to an
electrolytic cyanide recovery step (the overall cell
reaction; $CNS^- + 4H2O \rightarrow CN^- + H_2SO_4 + 3H_2$)(16) at a
future point in time. (Particularly so if the actual
RO concentration factor is close to 10:1)

d) HCN absorption

AVR Absorbors must handle efficiently
about 300 m^3/min air containing ~1500 x 10^{-6} mole
fraction HCN

AVR + RO Absorbor input (max.) is approximately
300 x 0.4 = 120 m^3/min air containing 3750 x 10^{-6} mole
fraction HCN

2) If RO could be applied successfully to the preconcentration of natural barren bleed (pH ~ 11) at approximately the same overall efficiency, then the added advantage would also accrue to the acidification slurry thickening step where thickener size requirements would be reduced. Precipitation phenomena may be affected.

CONCLUSIONS AND RECOMMENDATIONS

1. The AVR process should be pilot-plant tested, on-site, at any gold milling operation where any of the following factors are present:

   i) a large quantity of cyanide-containing components are discarded (or proposed as discard) on a daily basis. Significant capital or operating cost payback can be realized. If the quantity of solution to be processed, expressed as metric tonnes per kilogram of total cyanide content (CN_T) in solution, is within the range 3 to 5, then AVR should definitely be considered. If this ratio is less than 3 then very serious consideration should be given to the cyanide recovery process. The ratio is termed the treatment parameter (T.P.). The applicable ranges of this parameter (as it is applied to the volume of solution bled from the cyanidation circuit) are effectively increased in direct relationship to the concentration factor obtainable by reverse osmosis.

   ii) water discharge regulations are severe. This process provides for elimination of cyanide and unstabilized metal content from the barren bleed waste stream(s). No contaminants are added to the waste, either as reagent or as dissociation product(s). The CNS^- content in the final effluent exists in a very much simplified milieu. It may prove to be amenable to an electrolytic method for cyanide recovery (16) if reverse osmosis technology has increased the concentration to 2 g/L or more. Alternatively, the CNS^-, under these conditions, may be readily degraded by biological oxidation to yield $SO_4^=$, $CO_3^=$ and NO_3^- (17). The AVR effluent temperature profile would be quite acceptable for biological

activity. There would be no significant metal content to inhibit the efficiency of the biomass. The CNO^- content would also be degraded by the bacteria.

iii) water resource availability is restricted and/or costly. Substitution of reverse osmosis capability for a substantial portion of the capacity of the AVR process, would yield a quality water permeate, in large volume, for designated recycle.

2. The AVR process, representing a substantially-modified classical "acidification" process, should be initially piloted in the H_2SO_4-reagent mode. The acidification step is a simple one, requiring basic acidifier tank design.

3. AVR process control is very simple (pH) and is unaffected by the complex chemistry of the process. Some chemical control over species content has been discussed, conceptually, but the absolute requirement for it has not surfaced to date. It would be advantageous to manipulate process stoichiometry via recycle of <u>either</u> Cu^{++} or Fe^{++}/Fe^{+++} if, by doing so, the concentrations of ferro/ferri cyanide and tricyano cuprate (I) anions in the acidified barren bleed could be lowered by increasing the extent of copper/iron cyanide coprecipitation in weak acid milieu.

4. The AVR process is equally amenable to cyanide recovery when implemented in the SO_2-reagent mode. The addition of SO_2-scrubbing capacity, as accomplished by using scrub-acidifier towers, would be required. The increase in equipment cost may be more than offset by lowered reagent costs in locations where crude sulphur is readily available or roaster off-gas is an on-site reality. Operational parameters are such that oxidation of cyanide to cyanate does <u>not</u> take place. Duo-mode operation, utilizing SO_2 for partial acidification and H_2SO_4 for final pH adjustment, appears to offer possibilities for realization of reagent economies while limiting the requirement for tower-type acidifiers.

5. A novel and effective method is advocated for control of toxic, unstabilized precipitates which are formed within the process. Precipitate t-eatment technology is considered as an integral step of the process. The auxiliary step will be described in a separate report.

6. Although equipment requirements are greater for AVR than for oxidative destruction processes (eg., vapaerator units, HCN-absorbers and solid/liquid separation equipment), there are substantial off-setting benefits accruing to applicable mill operations. Very substantial cyanide recovery for reuse, and the capability for virtual elimination of all liquid and solid discard toxicity, are the two predominant advantages. The process represents a total package, flexible to changes in regulatory direction and adequate to the demands of the most environmentally-sensitive regions. In-situ "polishing" techniques are under investigation. Optimization should enable the final effluent to meet rigid regulations in regard to $[CN_T]$ and $[Me_T]$.

7. Investigation of the application of reverse osmosis technology to the AVR process is a priority. The potential for substantial economies to be realized in regard to overall capital costs is too great to be ignored. Processing efficiency improvement would also lower operating costs. In certain locations the improvement in water resource management could also provide economic return on investment. Industrially, reverse osmosis technology is at an advanced stage in regard to very high volume throughputs for certain types of contaminated waters.

8. Final effluent "polishing", if and when required could provide process security. The reneutralizer discharge which would normally be controlled to pH ≈ 9.5, and is a very low density slurry, may contain 1 to 2 mg/L copper plus nickel cyanides. At this pH, and considering the much simplified slurry matrix, the controlled addition of an oxidant may produce a very attractive benefit. It would appear to be possible to selectively oxidize, with controlled SO_2 or sulphite addition, the remnant of toxic content, concomitant with the

reneutralization step. This prospect should also be a priority assessment if the minesite location is in a heavily regulated region. Thiocyanate, one of the major components of the final AVR process effluent, would be unattacked by SO_2 (5), and so would not pose any additional reagent requirements. This effluent polishing concept would, of course, have to work at very low concentrations of metal cyanide. However, since the solution matrix is relatively simple, chemical interferences to oxidation would be expected to be minimal or non-existant.

If this proposed "polishing" step achieved the results hoped for, then the technique could be moved forward slightly into the process proper. That is, it could replace the last vapaerator unit and therefore become a treatment stage. This input to an oxidation stage could, logically, represent a CN_T value within the range 5 to 10 mg/L. Capital and energy costs would be recognizably reduced. Finally, efficient quality might be guaranteed.

The direct loss of recoverable cyanide would be less than two per cent. The metal recovery feature of the process would not be affected.

ACKNOWLEDGEMENTS

The author is most grateful for the continuously high level of cooperation and interest applied to this project by L.E. Carter, who assembled the test equipment, patiently modified the system as required, and was involved in all phases of the test program.

Appreciation is also expressed to K.G. Tan for the many valuable suggestions offered, particulary in regard to the theroetical aspects of this chemical process.

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APPENDIX 1

Figure 5 shows a detailed layout of an AVR facility which is designed to fully treat 1000 tonnes barren bleed per day for the recovery of all the cyanide content and all the major non-ferrous metal content.

Final wastes are innocuous solids plus water which will meet gold mill discharge specifications.

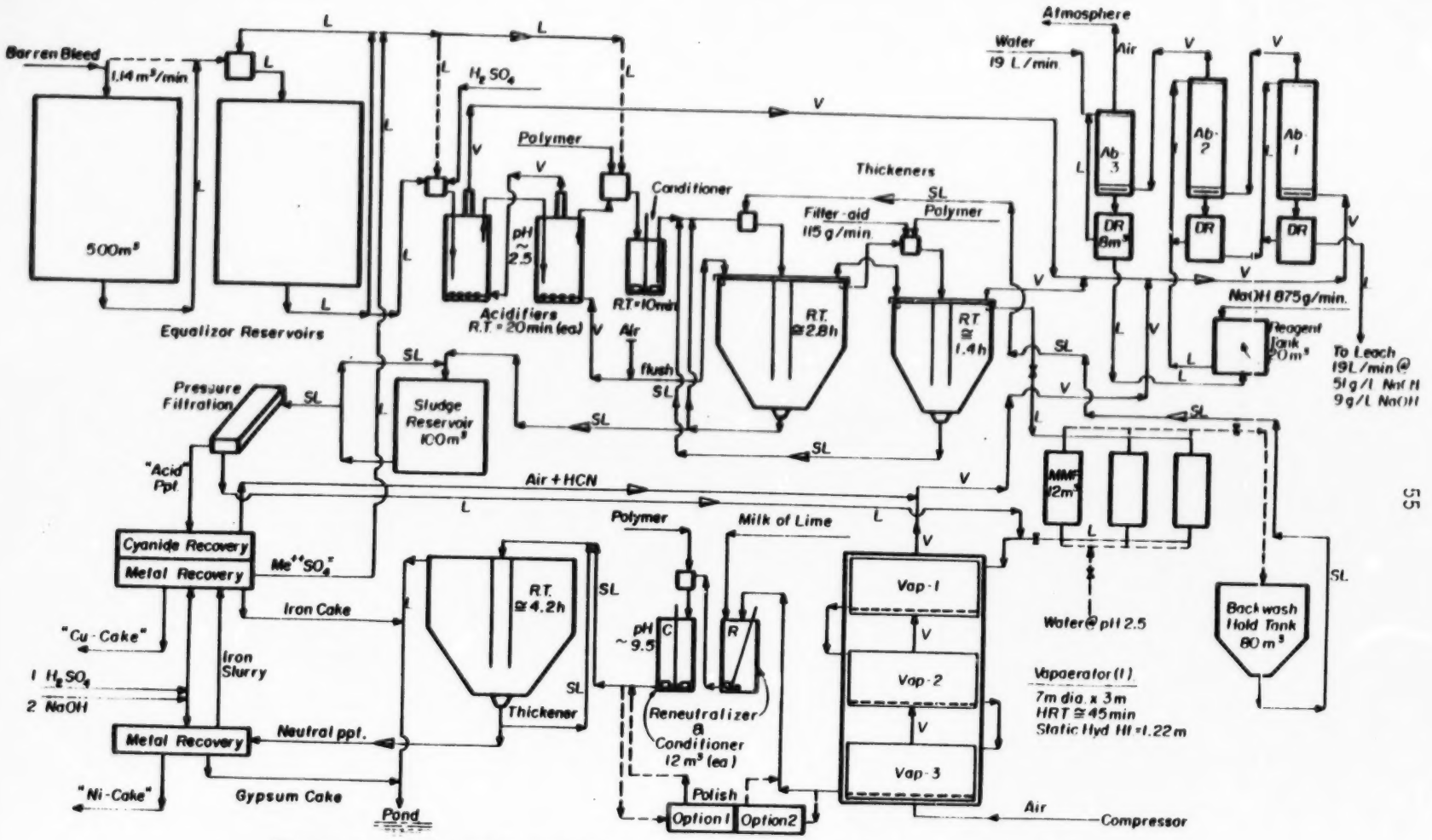

Figure 5 CYANIDE REGENERATION PROCESS FLOWSHEET: AVR–H_2SO_4

APPENDIX 2

The following unit operations equipment is designated as applicable to the AVR chemical process. Sizes are calculated for 1000 tonnes per day barren bleed input.

1. Acidifier - A reactor for destabilization and partial precipitation of metallo-cyanide complexes. Off-gases contained for directed flow.
   Size: approx. 8' dia. x 13' ht.

2. Thickener - A vessel or tank in which precipitate densification and liquid clarification are achieved

	Approx. dia. x ht.
"acid" thickener (#1)	21' x 23'
"acid" thickener (#2)	18' x 19'
"Neutral" thickener (#3)	26' x 23'

3. Vapaerator - reactor in which dissociation of soluble metallo-cyanide complexes is forced to completion by intensive aeration of the bulk liquid. Air acts as a carrier gas for volatilized HCN. Size: 23' dia. x 10' ht.

4. Absorber - tower containing polyethylene packing in which HCN gas and caustic (or milk of lime) are reacted to form NaCN (or $Ca(CN)_2$).
   Size: 6.5' dia. x 20' ht.

5. Equalizor - holding and blending tank which gives flexibility to the process by enabling recycled reactant (i.e., metal sulphate solution) to be equilibrated with barren bleed constituents, if required. A reservoir capacity for up to a one day supply of feed. Facilitates shutdown procedures.
   Size: 26' dia. x 33' ht.